WORKING PAPER

CHANGES IN VALUED "CAPACITIES"
OF SOILS AND SEDIMENTS AS INDICATORS
OF NONLINEAR AND TIME-DELAYED
ENVIRONMENTAL EFFECTS

William M. Stigliani

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IIASA
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for Applied Systems Analysis

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PREFACE

One of the objectives of IIASA's Study *The Future Environments for Europe: Some Implications of Alternative Development Paths* is to characterize nonlinear and time-delayed environmental effects that could be associated with plausible scenarios of Europe's socio-economic development over the next century. Early warning of such effects is only possible through an understanding of the key mechanisms that serve to regulate the dynamic, broad-scale changes occurring in the environment over time. Indeed, the failure in the past to foresee "sudden" ecological changes, such as forest dieback in Central Europe, stems largely from a lack of focus on the key regulators of change.

I believe this paper provides a major contribution to our current understanding of how soils and sediments respond to chemical inputs, and why the response is often manifested as a discontinuous ecological change. The strength of this paper is its treatment of the buffering, sorption, and oxygen-donating capacities of soils and sediments, not as separate entities, but rather, as interlinked properties. It thereby synthesizes ideas that have usually been discussed independently, and demonstrates, in fact, that our understanding of ecological change in soils and sediments is limited unless we also comprehend the full range of interactions between these capacities.

R. E. Munn
Leader, Environment Program

ACKNOWLEDGMENT

ABSTRACT

This paper discusses the buffering, oxygen-donating, and sorption capacities of soils and sediments as an inter-connected system for regulating the retention and release of chemical pollutants. In this context, the author discusses the chemical conditions under which sediments may serve as a source or a sink for toxic materials, and conditions under which soils may retain or release them. It is demonstrated that nonlinear, time-delayed ecological transformations in soils and sediments often can be understood in terms of the interlinked system. The author discusses some possible future long-term environmental problems that might beset Europe, and some implications for a monitoring strategy for foreseeing such problems.

Because the release of adsorbed toxic chemicals from heavily polluted sediments and soils can occur suddenly owing to changes in oxygen status (i.e., redox potential) or acidity, strategies for preventing the long-term release of such materials should not only consider current conditions of pH and redox potential, but also, how those conditions might change in the future.

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CHANGES IN VALUED "CAPACITIES" OF SOILS AND SEDIMENTS AS INDICATORS OF NONLINEAR AND TIME-DELAYED ENVIRONMENTAL EFFECTS

William M. Stigliani

1. INTRODUCTION

Recently, investigators have reported a trend of increasing mercury content in fish in Swedish lakes, even though there has been a significant decrease in mercury emissions from Swedish industries in the last two decades (Hakanson et al., 1988). In commenting on this trend, the authors note that "old Swedish 'sins' are still causing a lot of problems." Lakes in Ontario continue to acidify even though deposition of SO_4^{-2} and H^+ are decreasing (Dillon et al., 1987). Sudden and unprecedented dieback of forests has occurred in countries such as West Germany, Switzerland, Austria and Czechoslovakia since the early 1980s even though emissions of most major air pollutants in the region have been stable or declining since the mid-1970s (IIASA, 1988).

Such occurrences suggest that: 1) environmental effects may be displaced in time from the activities that cause them; and 2) even when reductions in polluting emissions are enacted, environmental effects may still occur owing to the steady accumulation of polluting materials in the environment over previous decades. Policy makers and the public alike may be surprised by the onset of such recently observed deteriorations in the environment, since prevailing wisdom and common sense might suggest that an era of lowered emissions of polluting materials to the environment should be accompanied by an improvement in its state, rather than a worsening of it.

However, as has been indicated by Brooks (1986), industrial societies gain certain socio-economic "benefits" from broad-scale applications of technologies, but such benefits are often accompanied by "disbenefits" to the environment and society as a whole. Brooks further asserts that the manifestation of benefits and disbenefits may be characteristically different in two important respects. Firstly, whereas benefits are usually directly proportional to the scale of application of the technology, disbenefits may vary nonlinearly with scale. (See Figure 1.) Secondly, benefits are typically manifested on "fast" timescales, while disbenefits may become obvious only on relatively "slow" timescales. These differences are highly significant because, as noted by Brooks, "a technological activity may become strongly established with influential vested interests during the linear regime, before the disbenefits that increase nonlinearly with scale begin to manifest themselves or become apparent to a wider public".

The purpose of this paper is to explore the aspects of nonlinear ecological behavior and the apparent mismatch of timescales between economic activities and ecological effects. I will explore these aspects from the viewpoint of changes in three important physiochemical "capacities" of soils and sediments; namely, the capacities to buffer acidity, donate oxygen, and adsorb ambient chemical materials. The first two capacities are particularly relevant environmental determinants because they are among the most important chemical factors mediating the speciation, solubility, and bioavailability of toxic and ecologically harmful chemicals in the environment. Physical adsorption capacity is also of

great environmental significance because it determines the ability of soils and sediments to store or release toxic materials and nutrients.

Each one of these capacities will be described in turn, with examples of how they mediate the environment's response to given anthropogenic chemical inputs. In a later section of this paper, the author describes some of the implications of the findings in terms of linkages between specific human activities and nonlinear ecological changes, including a sampler of development-environment interactions that might emerge as important in the future. The final section is a discussion of how one may incorporate historical information and some imaginative speculation about future environmental changes into the design of a more robust monitoring system for providing early warning of certain impending environmental changes.

The focus of much of the discussion is the European environment, since this paper is in support of an ongoing study at IIASA on the Future Environments for Europe: Some Implications of Alternative Development Paths.

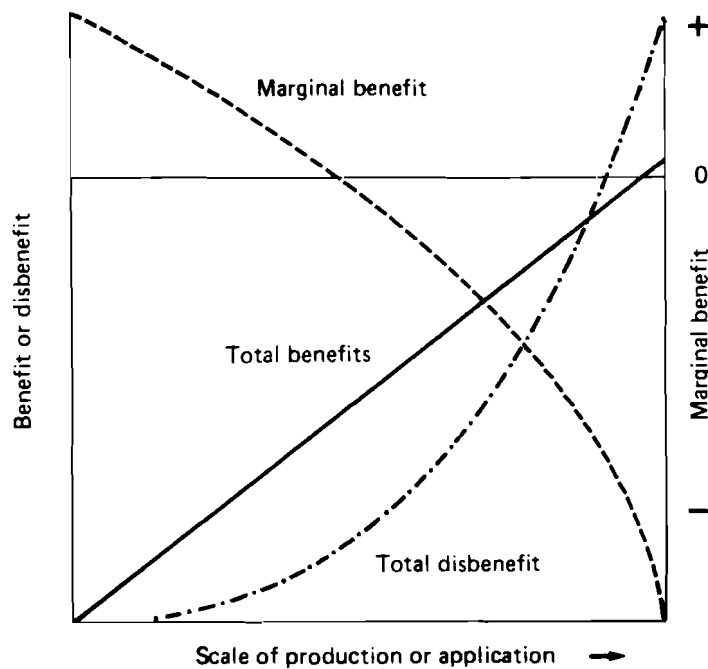*Figure 1*   Variation of benefits and disbenefits of a technology with scale of application. The solid curve and the dot-dashed curve show the benefits (linear) and the disbenefits (nonlinear), respectively, while the dashed curve shows the net marginal benefit as a function of scale (essentially the derivative of the difference between the benefit and the disbenefit curves). Source: Brooks, 1986.

2. THE SOIL'S CAPACITY FOR BUFFERING AGAINST ACIDIC INPUTS

An important attribute of many soils is their capacity to neutralize (i.e.; buffer) acids. This capacity plays an essential role in maintaining the stability of fresh water habitats, since soils in the watersheds of lakes serve to stabilize the pH of the lake waters over a wide range of acid inputs, thus protecting fish and other aquatic life from large fluctuations in acidity. Soils vary greatly in their ability to neutralize acids. The most poorly buffered soils are those on low-weathering siliceous bedrock, quartzites, sandstones, granites, and felsic gneisses, each of which has a low capacity to replenish alkaline substances lost in acid-neurtralization reactions.

2.1. Historical Perspective

Over the last 100 to 150 years in many regions of the industrialized countries of North America and Europe, large perturbations of the soils' buffering capacities have occurred, resulting from atmospheric deposition of sulfuric and nitric acids generated during the burning of fossil fuels. Because of the large variability in soil types, even over small spatial scales, the effects on soils and water bodies from acidic atmospheric inputs are not uniform. Nevertheless, regional distinctions can be made. Two representative areas with soils low in buffering capacity are the Adirondack Mountains of the United States and Scandinavia. Also described in this paper is the situation in Central Europe. Soils there are generally more resistant to acidification than those in Scandinavia, but because acidic inputs are as much as an order of magnitude higher in Central Europe, its soils are currently even more vulnerable.

A conceptual framework for describing the relative vulnerability of lakes to acidification is illustrated in Figure 2. Watershed soils are grouped according to two fundamental qualities for buffering against atmospheric deposition from sulfuric acid--the ability to retain sulfate, and the ability to supply base cations (NRC 1984). Lakes and streams with watershed soils having both a low ability to retain sulfate inputs and a low ability to release base cations will respond quickly to changes in acid deposition (say on the order of a few years to 20 years). Conversely, lakes and streams associated with watershed soils having very large abilities to retain sulfate and to release base cations may exhibit no response to acidification (on the order of centuries to millenia). Between these two extreme cases are watershed soils having a moderate ability to retain sulfate and/or to release base cations. Such lakes will exhibit a delayed response to acidification (on the order of decades or longer).

Most lakes in North America and Europe are in the "delayed response" category. In order to determine the time of the response of lakes to acidic inputs it is necessary to know the history of emissions upwind from the affected lake, the time trend in lake pH, and the trend in the depletion of the buffering capacity of the soils in the watershed. Unfortunately, there is little precise historical information available in the literature. Big Moose Lake, in the Adirondack Mountains of New York State, is one of the few examples where accurate, simultaneous information exists for trends in pH, SO_2 emissions, and fish populations. (See Figure 3.) One may observe that the pH of the lake remained essentially constant (except for a slight decline due to natural senescence) over the entire period from 1760 to 1950. Then, within the space of 30 years (1950 to 1980), the pH of the lake declined more than one whole pH unit (corresponding to a factor of 10 increase in acidity). One may notice that the onset of the decline in pH was not synchronous to the onset of emissions of sulfur. Rather, it occurred 70 years after the beginning of SO_2 emissions and 30 years after the emissions had peaked at around 1920. In the 70 years between 1880 and 1950 an estimated 50 grams of sulfur/sq. meter and 2.5 to 3 grams of
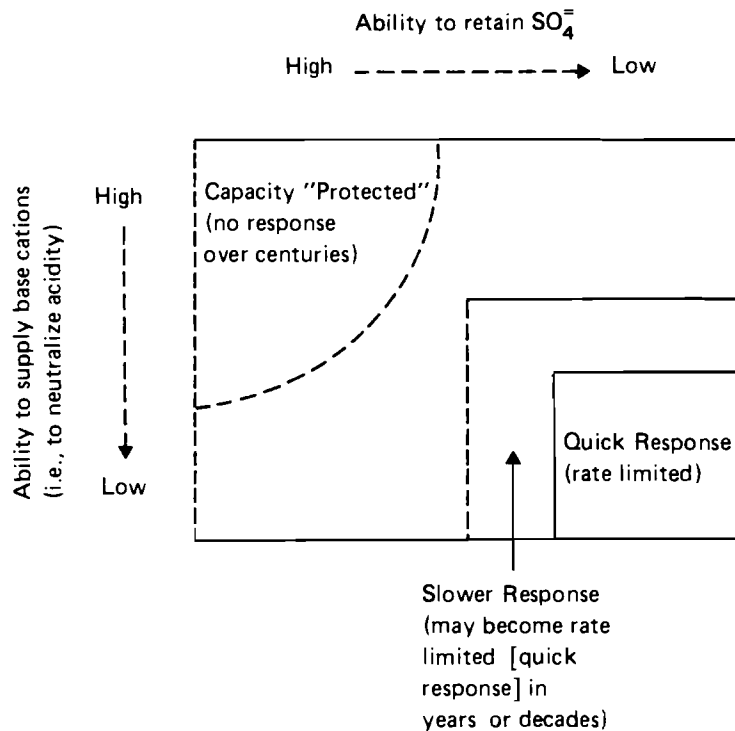
Ability to retain SO$_4^=$

High _ _ _ _ _ _ _ _ _ → Low

Ability to supply base cations
(i.e., to neutralize acidity)

High

Low

Capacity "Protected"
(no response
over centuries)

Quick Response
(rate limited)

Slower Response
(may become rate
limited [quick
response] in
years or decades)

Figure 2   A qualitative presentation of the effect of two major soil properties--the ability to retain sulfate and the ability to supply base cations--on the rate at which streams and lakes respond to changes in acid deposition. Source: NRC, 1984.

hydrogen/sq. meter were deposited in the watershed of Big Moose Lake.[1] These quantities were apparently great enough to deplete the sulfate retention and cation release capacities of the soils over this time span. Thus, beginning around 1950 atmospheric acid deposition moved through the buffer-depleted soils and percolated into the lake with little or no neutralization. At that point, acid sensitive fish species such as smallmouth bass, whitefish, and longnose sucker began to disappear, followed in the late 1960s by the more acid-resistant lake trout.

The history of the acidification of Big Moose Lake clearly demonstrates Brooks' hypothesis of benefits and disbenefits from application of technologies. The benefits of coal burning in the Ohio Valley, upwind from Big Moose Lake, in terms of greatly increased industrial productivity and expanded electric power production exemplifies the "tendency of sociotechnical systems to respond preferentially to 'fast variables' in the environment, as compared to 'slow variables', especially when the latter are less familiar or predictable" (Brooks 1986). In this case the slow variable was the gradual depletion of buffering capacity in the watershed soils. It was not until the 1970s, nearly 100 years after the advent of coal burning in North America, that the "disbenefits" of coal combustion related to acid deposition became a matter of national concern.

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[1]This estimate is based on the assumption that the annual wet depositions of sulfur and hydrogen at Big Moose Lake over the period from 1920 to 1980 was equal to the values for 1980, which were about 1.1 and 0.06 grams/square meter, respectively. Total wet depositions from 1880 to 1920 were obtained by integration of the emission curve shown in Figure 3.
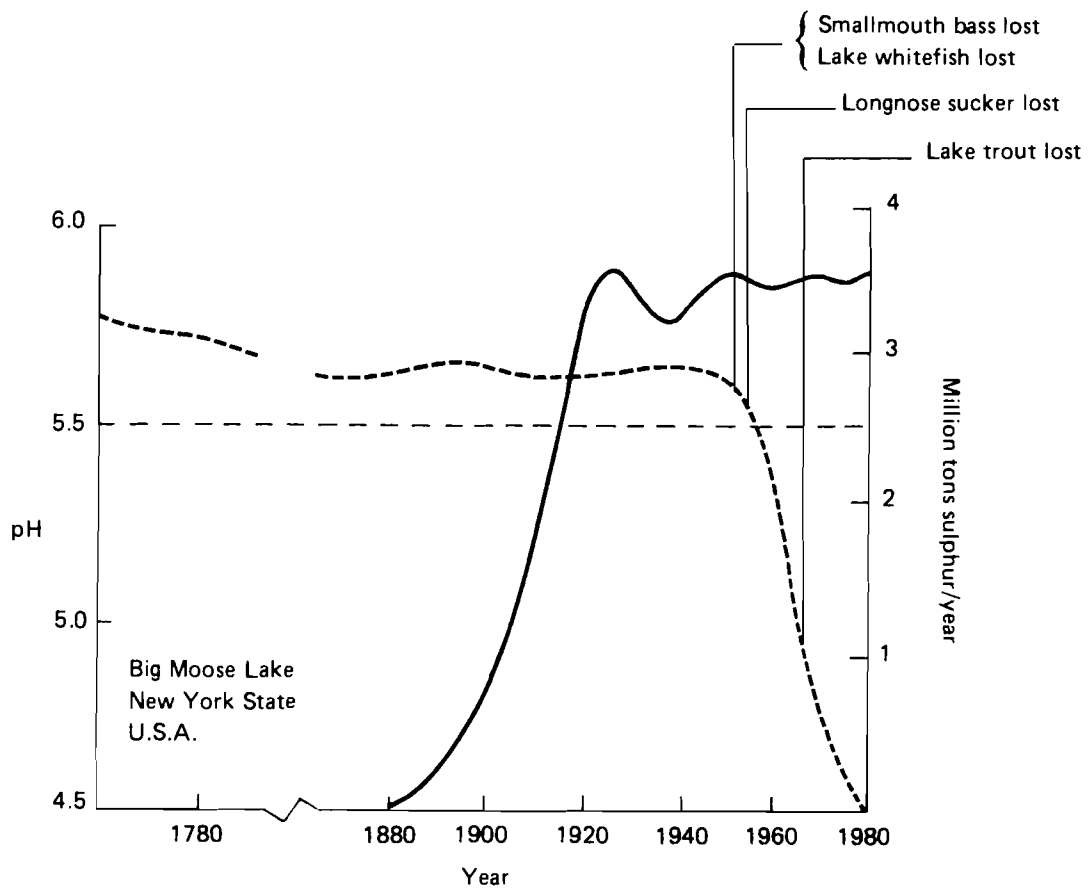
Figure 3   Trends in pH (dashed line), emissions of SO$_2$ upwind from the lake (solid line), and fish extinctions for the period from 1760 to 1980. The pH history was reconstructed by analyzing diatom assemblages in sediment core samples (Charles and Norton, 1986). The history of emissions of SO$_2$ upwind from the lake was estimated from data on fuel consumption and sulfur content in coal consumed (Husar 1986). The history of fish species extinctions was tabulated by Haines, 1986.

The experience in Europe has been similar to that in the U.S.A. The first area to udergo widespread lake acidity was southern Scandinavia, where many of the watersheds are on igneous bedrock with a very low buffering capacity. Acidification of fresh waters was noticed in southern Norway as early as the 1920s, causing lower yields of salmon in some large rivers. (See Figure 4.) By then, these rivers occasionally showed pH values below 5.5, and present values are often below 5.0. In Sweden the first biological symptoms of acidification were noticed in the 1920s and 1930s, with a decrease in number of the most sensitive fish species (roach) in some very poorly buffered lakes with pH values below 6 during summer. Currently, these lakes are the most acidic in Sweden, with pH values of 4.0 to 4.5 or even less (Almer et al., 1978).

Several historical comparative studies of soil acidification in southern and southwestern Sweden have been conducted recently (Tamm and Hallbaecken, 1988; Andersson, 1986; Tyler et al., 1985). Each of these studies indicates a general trend toward acidification on the order of 0.5 to 0.7 pH units. Tyler et al., in a study of 230 deciduous forests in Skane, the southernmost part of Sweden, concluded that the pH of

TONS   68 RIVERS

TONS   7 ACID RIVERS
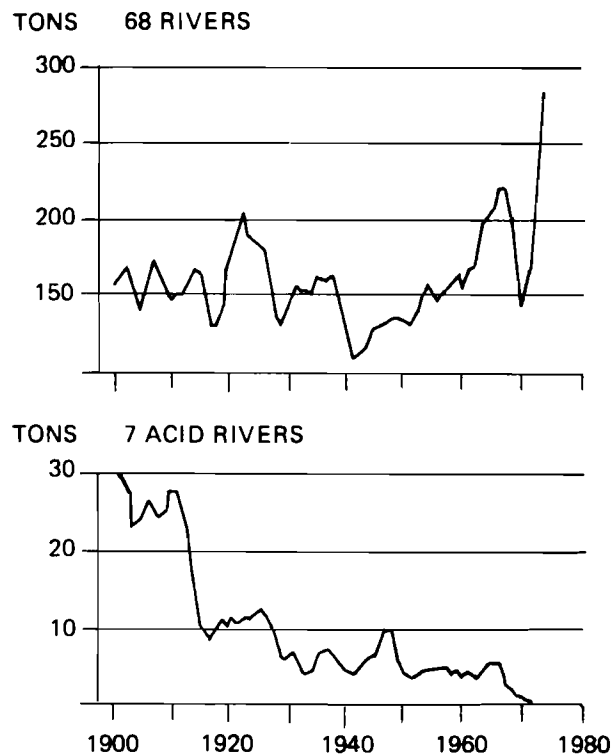
Figure 4   Norwegian salmon fishery statistics for 68 unacidified and 7 acidified rivers. Source: Braekke, 1976.

the humus layer decreased by about 0.7 pH units since 1949. (See Figure 5). It was further noted (Andersson, 1986) that this decrease corresponds to a change in base saturation of approximately 50%; this means that about half of the sum of the basic cations has been replaced by H^+ and Al^{+3} over this period. Tamm and Hallbaecken compared changes in soil acidity since the 1920s in two coniferous forests, one in northern Sweden where acid deposition has traditionally been low, and the other in southwestern Sweden receiving relatively high inputs of acid deposition. The authors demonstrated that the pH of the subsoils (B and C horizons) in the northern forest did not change significantly between 1926 and 1985. However, in the southwestern forest there was a significant trend toward acidification, especially in the C horizon, (at 70-cm depth) for which a decrease of 0.5 to 0.7 pH units was calculated between 1927 to 1982- 1984.[2]

2.2. Potential Vulnerabilities in the Future

In comparison, Central European soils have been more resistant to acidification. Nevertheless, with current sulfur deposition rates as much as ten times higher in Central

[2]The authors of the cited papers were well aware of the widely accepted view that the acidity of the upper soil horizons (the humus layer and the bleached horizon of podsol profiles) is strongly affected by the dominating tree species and by the age of the stand. These factors were taken into account in arriving at the final conclusion that acid deposition was the most likely cause of extensive acidification, especially in the deep soil horizons. See cited papers for details.
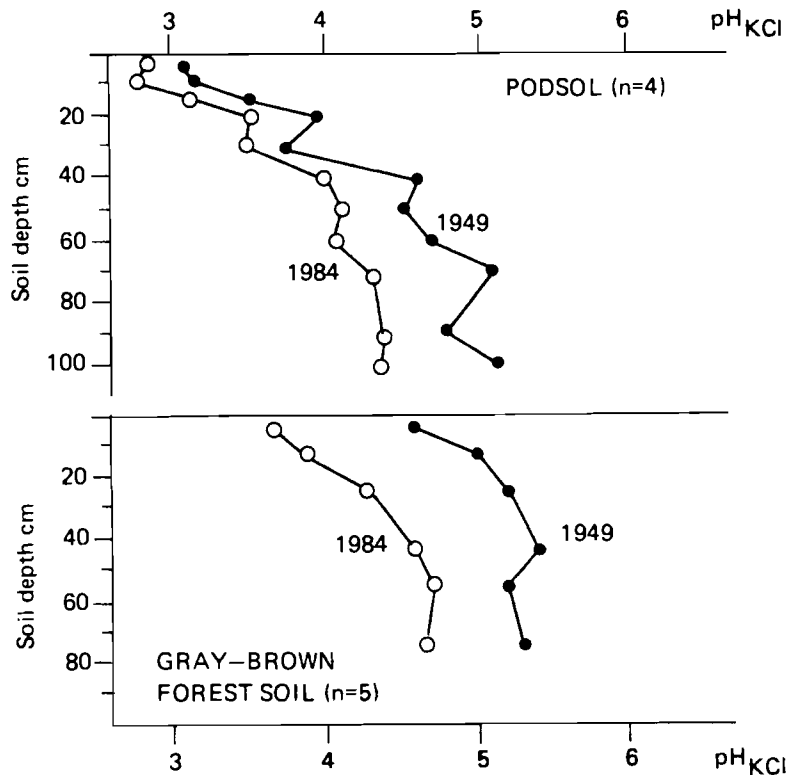
Figure 5   The pH changes at different depths between 1949 and 1984 in forest soils of southernmost Sweden. Source: Tyler et al., 1985.

Europe than are the rates in southern Sweden,[3] the buffering capacities of many of these soils have reached, or will reach in the coming decades, their limits for neutralizing acids (Alcamo et al. 1987). Figure 6 depicts the percentage of forest soils in the next 50 years in Central Europe that may have a pH less than 4 under various emission scenarios. One may observe that even under the current multinational agreement, endorsed by most European countries, for reducing sulfur emissions by 30% relative to 1980 emissions (effective as of 1993), the soils will still be highly vulnerable to acidification.

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[3]In some parts of East Germany, Czechoslovakia, and Poland, sulfur deposition levels exceeded 10 grams/sq. meter in 1980. Most of southern Scandinavia experienced deposition levels of 1 to 2 grams/sq. meter, and a rather small area in the southern extremities experienced levels of 2 to 3 grams/sq. meter (Alcamo et al., 1987).

- 8 -

60

50

40

Percent of area

30

20

10

30% Reduction All Europe
Scenario

Major Sulfur Controls
Scenario

$5\ g \cdot m^{-2} \cdot yr^{-1}$ Deposition Limit
Scenario

1960 1970 1980 1990 2000 2010 2020 2030 2040

Time (years)
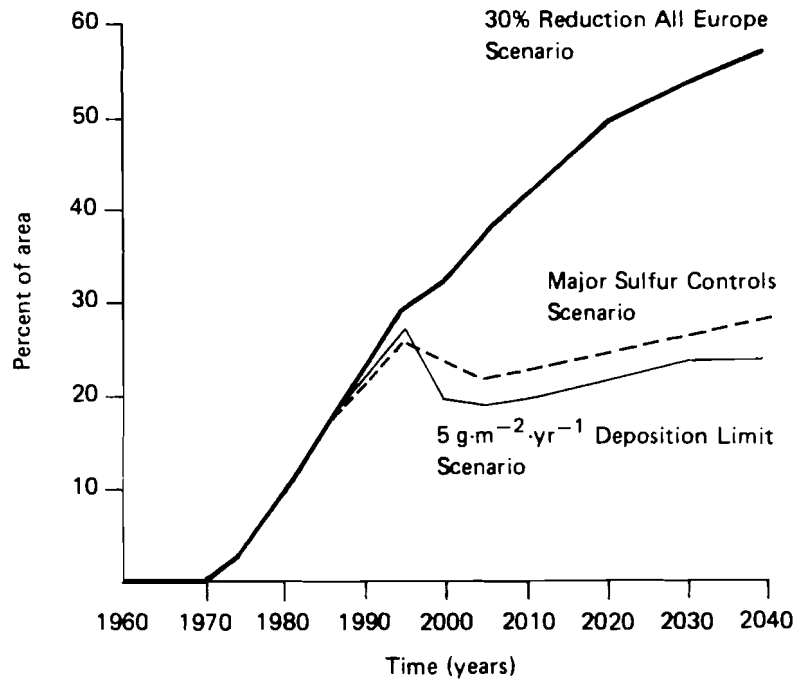
Figure 6   Percentage of Central European forest soils with pH less than 4.0 for three scenarios. The 30% Reduction Scenario (relative to 1980 sulfur emissions) is already in effect for most European countries. The Major Sulfur Control Scenario assumes implementation in all European countries of strong pollution control measures including flue gas desulfurization in stationary sources (with 90% SO_2 removal efficiency), and SO_2 reduction efficiencies of 50% in mobile sources. The Deposition Limit Scenario is a cost optimal solution for reducing the maximum deposition level within Europe to 5 $g/m^2/yr$. See source for details. Central Europe is defined as East and West Germany, Poland, Czechoslovakia, Hungary, Austria, and Switzerland. Source: Alcamo et al., 1987.

3. THE SOIL'S CAPACITY TO ADSORB PHOSPHORUS AND TOXIC MATERIALS

When chemicals are added to soils, either inadvertently or deliberately, their fates are partitioned among four possible pathways. As shown in Figure 7, chemicals (or their degradation products) may leach rapidly through the soil into ground and surface waters, they may be taken up by crops and other vegetation, they may volatilize into the atmosphere, or they may be retained and stored in the soil. For the first three pathways, if the chemicals are deleterious to the environment, observable effects may be noted, often within a short period of time after application. Nitrogen fertilizer is a prime example of an easily leachable chemical that has caused very serious water quality problems in Europe and elsewhere. Regarding pathway 2, the uptake by crops of toxic materials has long been a public health concern, especially in farm areas fertilized by sewage sludge and animal wastes found to be contaminated with such chemicals (Sauerbeck, 1987). Volatile pesticides used in soil fumigation are a widely used class of chemicals following pathway 3. Occasionally, fumigants have caused air quality problems in areas in close proximity to the site of application. (See Huygen and van Ijssel, 1981 for the case of methyl-bromide.)

It is pathway 4, however, that is of most interest in terms of the potential for non-linear and time-delayed environmental effects. For as long as the chemical is stored in the soil, it may exhibit little or no ostensible effect. However, the potential danger of chemicals so retained is that they may tend to accumulate, and be released as some threshold is reached for the soil's capacity to hold the chemical. In this section we describe some important chemicals that interact with soils in this way.
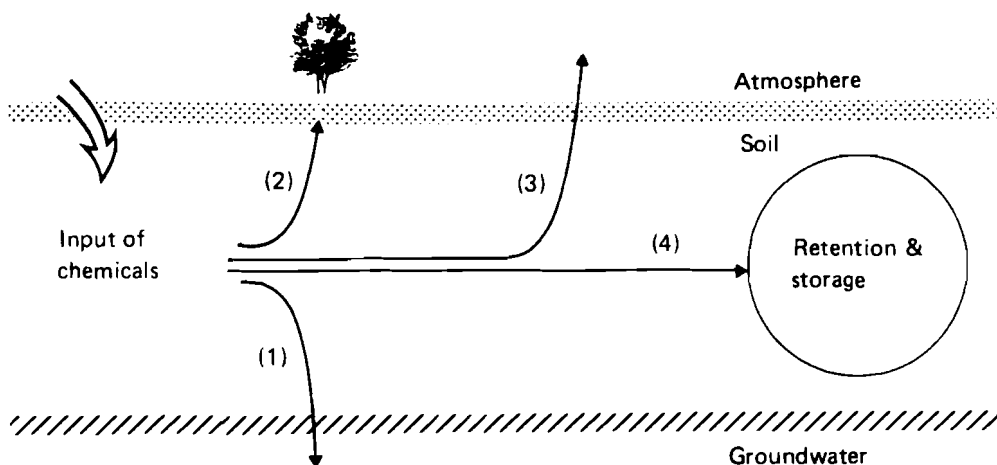
Figure 7   Pathways of chemical inputs to soils. Pathway 1 is rapid leaching through soils into water courses; 2 is uptake by plants; 3 is volatilization to the atmosphere; and 4 is storage and retention in soil.

3.1. Phosphorus

Under natural conditions, phosphorus and nitrogen are normally limiting nutrients in crop production. Beginning in the years shortly after the Second World War, farmers in industrialized countries were able to circumvent this limitation by the application of ever-increasing amounts of synthetically produced nitrogen and phosphorus fertilizers to agricultural soils. As shown in Figure 8, the results in terms of increased productivity were spectacular. However, a heavy price in terms of degradation of the environment has been paid for the increased crop yield. The major cause of this degradation has been the

excess quantities of nutrients that have been applied to sustain the yields. In order to ensure that nutrient uptake by crops is maximized, large quantities are typically applied early in the growing season. But uptake is far from complete for either nutrient. Much of the nitrogen is lost to the environment by rapid leaching through the soils into ground and surface waters, and by denitrification to the atmosphere. In contrast, phosphates do not leach rapidly through soils. Rather, a large fraction of the phosphates are adsorbed quite strongly on the surfaces of soil particles, and are thus unavailable for plant uptake.
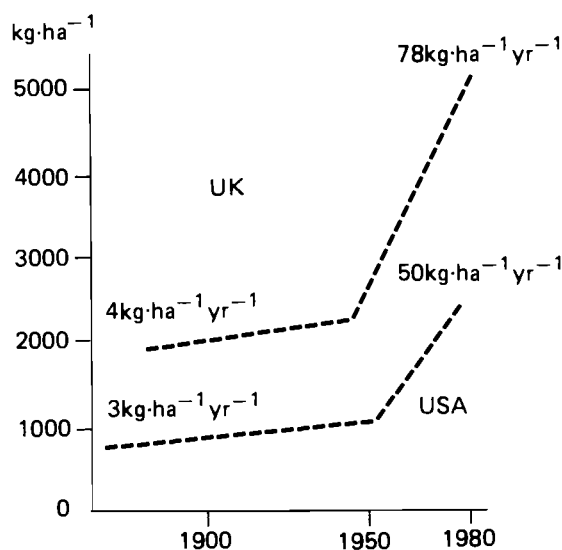
Figure 8   The trends in the yield of wheat in the United States and the United Kingdom over the last 100 years. Numbers refer to increases in yields per year. Trends are generally indicative of crop yields in other industrialized countries as well. Source: FAO data and De Wit, 1981.

The effects of nitrogen leaching (in the form of nitrate) into groundwaters have been well documented over the last two decades. (See for example Schroder, 1985.) A less well-known and less studied problem, but one that may prove to be equally as detrimental over the long term, is the potential for saturation of phosphorus in agricultural soils, and its subsequent leaching into water bodies. Because phosphorus is often the limiting nutrient in natural water systems, even small increases of phosphorus inputs may lead to greatly increased rates of eutrophication of lakes, streams, and rivers. In the 1970s, eutrophication caused by the release of phosphorus in domestic sewage, mainly from phosphate additives in detergents, was a well-publicized political issue. Consequently, sewage treatment systems for removing phosphorus evolved quickly. In the case of Sweden and Finland, a phosphorus removal efficiency of over 90% was achieved by the early 1980s (L. Kauppi, IIASA, personal communication, 1988).

Currently, eutrophication from phosphorus loading is hardly mentioned as a major environmental issue. This general lack of concern may be yet another example whereby the highest priorities for protecting the environment are directed at short-term problems, rather than those that are only manifested over the long-term. The fact is that agriculture is by far the major consumer of phosphorus in Europe. During the growing season of 1984-1985 over 3.5 million tons were consumed in fertilizer application. (One may compare this amount to the approximately 0.7 million tons used in detergents.) Moreover, Behrendt (1988) has estimated that approximately 50% to 60% of the applied phosphorus

is stored in the soils, with the balance absorbed by plant uptake. While generally, there is no immediate problem of phosphorus leaching to water courses, over a period of decades accumulation may eventually exhaust the soil's adsorption capacity.

This finite ability of soils to store phosphorus is defined quantitatively by an index called the phosphate sorption capacity (PSC). As shown in Figure 9, the soil may be depicted as a reservoir for phosphorus inputs. As long as the reservoir is unsaturated, outputs (i.e., leaching of phosphorus from the soil system) are either not observed or minimal. But as soils become saturated with phosphorus, even small inputs may cause significant amounts of phosphate to "leak" from the reservoir. The time delay before effects can be observed is dependent on two factors; the rate of input (P_I), and the size of the reservoir (R). One may observe from this simple model another example of a possible delayed-response, discontinuous environmental change operating over a slow timescale.
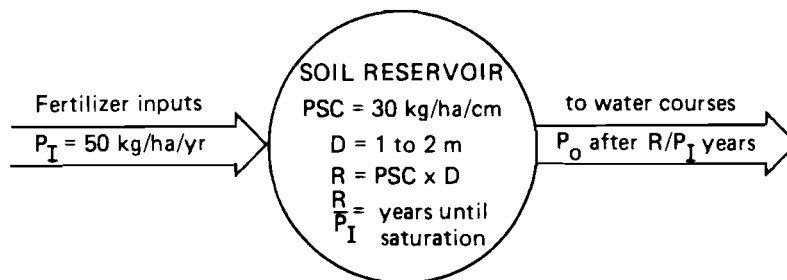
Figure 9   Schematic representation of phosphorus inputs/outputs and the time delay until phosphorus leaches from agricultural soils. P_I is the phosphorus input; D is the depth of the water table underneath the soil; R is the storage capacity of the reservoir; R/P_I is the time required for the reservoir to reach saturation; P_0 is the phosphorus output. The values assigned to these parameters are representative of many agricultural regions in Europe. Note that for D between 1 and 2 meters, R/P_I is 60 to 120 years. Phosphorus has already been accumulating in European soils for approximately 40 years.

In practice, the PSC varies according to soil type and water-table class. There are few precise measurements of PCS, although Dutch investigators have recently calculated values for five sandy soil types in the Netherlands as a function of water-table class (Breeuwsma and Schoumans, 1987). These values ranged from 3.7 to 77 kg P/ha/cm, with a mean value of 22.7 and a median value of 21.6 kg P/ha/cm. Currently, most agricultural soils in Europe are not phosphate-saturated. However, when viewed over a time horizon of decades to a century, and assuming current phosphate application rates, phosphate leaching is a distinct possibility, especially from soils having high inputs, low values of PSC and high water tables.

A preview of what could be in store for other areas of Europe may be gained by taking note of what is occurring now in probably the most vulnerable area on the continent for phosphate saturation. This is the area of intensive livestock feeding in the Netherlands, where exceedingly high levels of manure, corresponding to average values of phosphorus application on the order of 220 - 440 kg phosphorus/ha/ yr,[4] have been applied to

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[4]In contrast, the highest levels of phosphorus application in normal agricultural practice in Europe are about 80 kg/ha/yr, but more typical application levels are approximately 50 kg/ha/year or less.

sandy soils at local farms. In these limited areas, extensive phosphorus saturation has already been observed (Breeuwsma and Schoumans, 1987). Figure 10 gives an estimate of the spreading of phosphate saturation in this area given certain application scenarios.
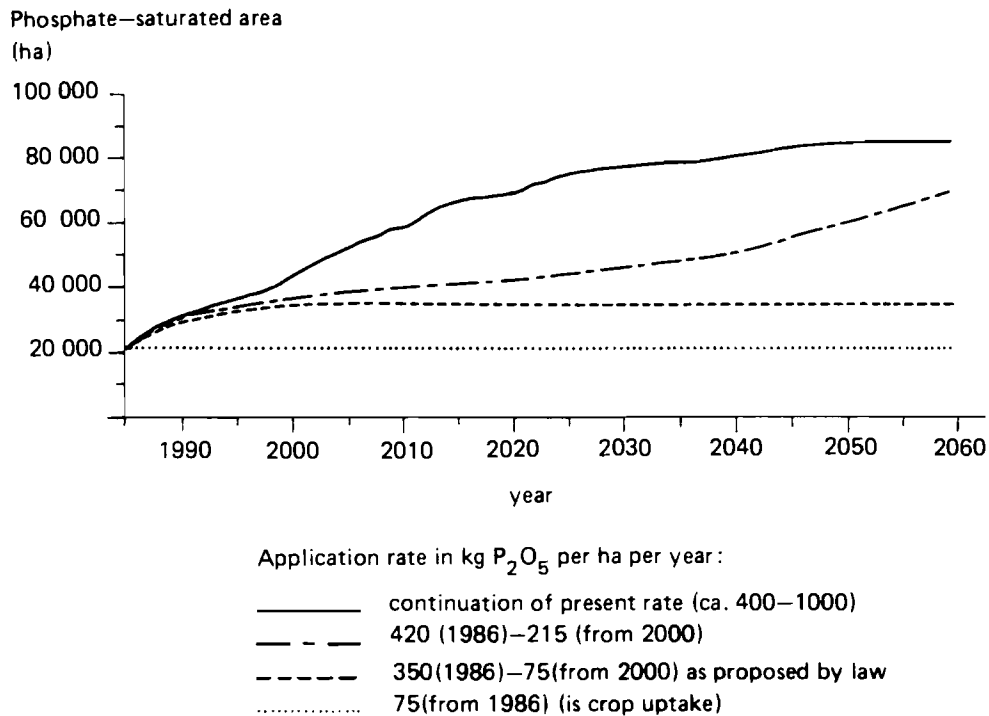
Phosphate—saturated area
(ha)

Application rate in kg P_2O_5 per ha per year:

———————	continuation of present rate (ca. 400—1000)
— — —	420 (1986)—215 (from 2000)
— — — —	350(1986)—75(from 2000) as proposed by law
....	75(from 1986) (is crop uptake)

Figure 10 Long-term extension of the area of phosphate-saturated maize land in the Netherlands for four scenarios of phosphate application. Source: Breeuwsma and Schoumans, 1987.

Behrendt (1988) has calculated possible scenarios of phosphate enrichment of agricultural soils in The Netherlands, the Federal Republic of Germany, the German Democratic Republic, and Denmark until the year 2080. Based on national statistics for phosphate use and crop yields, the results may be useful in indicating potential vulnerabilities to future phosphorus leaching. Figure 11 shows the trend of inputs of phosphorus fertilizer, outputs (by crop), and the difference (phosphorus assumed to be stored in the soil) for agricultural development in the Netherlands from 1945 to 1985. The other countries in the analysis show similar trends, although inputs, outputs and differences are all less than those for Dutch agriculture. One can observe from the Figure that there has been a steadily increasing rate of phosphorus accumulation over the 40 year period. Given a natural content of phosphorus in soils of approximately 1600 kg/ha, the author estimated that the phosphorus content of soils increased in a range between 40% (in Denmark) to 85% (in the Netherlands) during this time. Figure 12 projects these accumulations up to the year 2080, assuming a continuance of current rates of application. The analysis estimates a maximum of a four-fold increase of phosphorus content in Dutch soils and a minimum of two-fold increase in Danish soils. Assuming a PSC value of 30 kg P/ha/cm, the calculation shows that the upper one to two meters of soil would be saturated. Based on this analysis, Behrendt estimates that it is possible that more than 10% of agricultural areas of the investigated countries, specifically those areas with high water tables, low values of PSC, and high application rates of phosphorus, may be vulnerable to phosphate leaching.
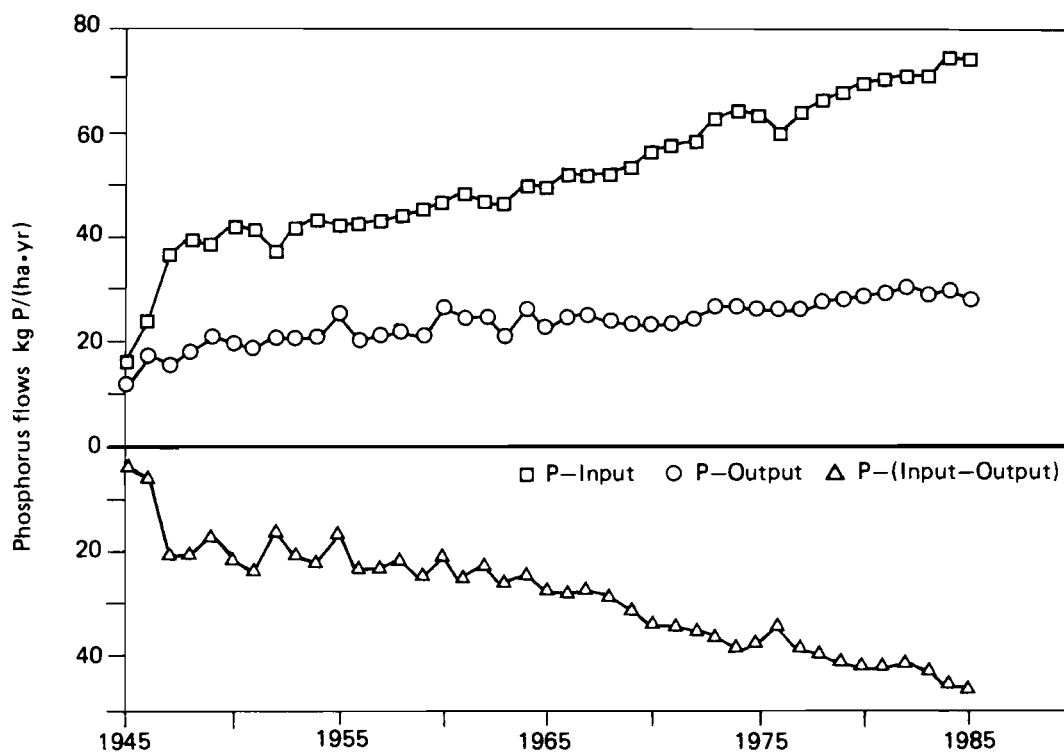
Figure 11   Estimated trends in inputs and outputs for phosphorus use in agriculture in the Netherlands from 1945 to 1985. P-inputs are for fertilizer and manure application; P-outputs are for phosphorus uptake by plants; P-(input-output) is phosphorus stored in the soil. Source: Behrendt, 1988.

3.2. Toxic Materials in Agricultural Soils

Agricultural soils have been the recipient of large inputs of toxic materials from the addition of pesticides and contaminated fertilizers. (See Sauerbeck, 1987 for a detailed review.) As described previously, some of this material has a rather short life-time in the soil due to leaching, volatilization, or uptake by plants. However, a substantial amount remains stored in the soil. This is especially true of certain heavy metals and organic pesticides, that are present in the soils either as insoluble products or as sorbed entities on the surfaces of soil substrates. The mechanisms of retention are complex, depending on soil type, and the physical and chemical conditions in the soil environment.

One of the major properties of soils that contributes to their ability of adsorb and store heavy metals is the presence of cation (i.e., positive ion) exchange sites on their surfaces. Cation exchange may occur when a heavy metal ion exchanges with some other ion that initially occupied an adsorption site on a soil particle. For example, in clay soils heavy metal cations (M^{+2}) often exchange with Ca^{+2}:

$$M^{+2} + clay-Ca \rightarrow Ca^{+2} + clay-M$$
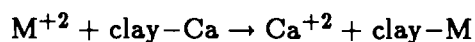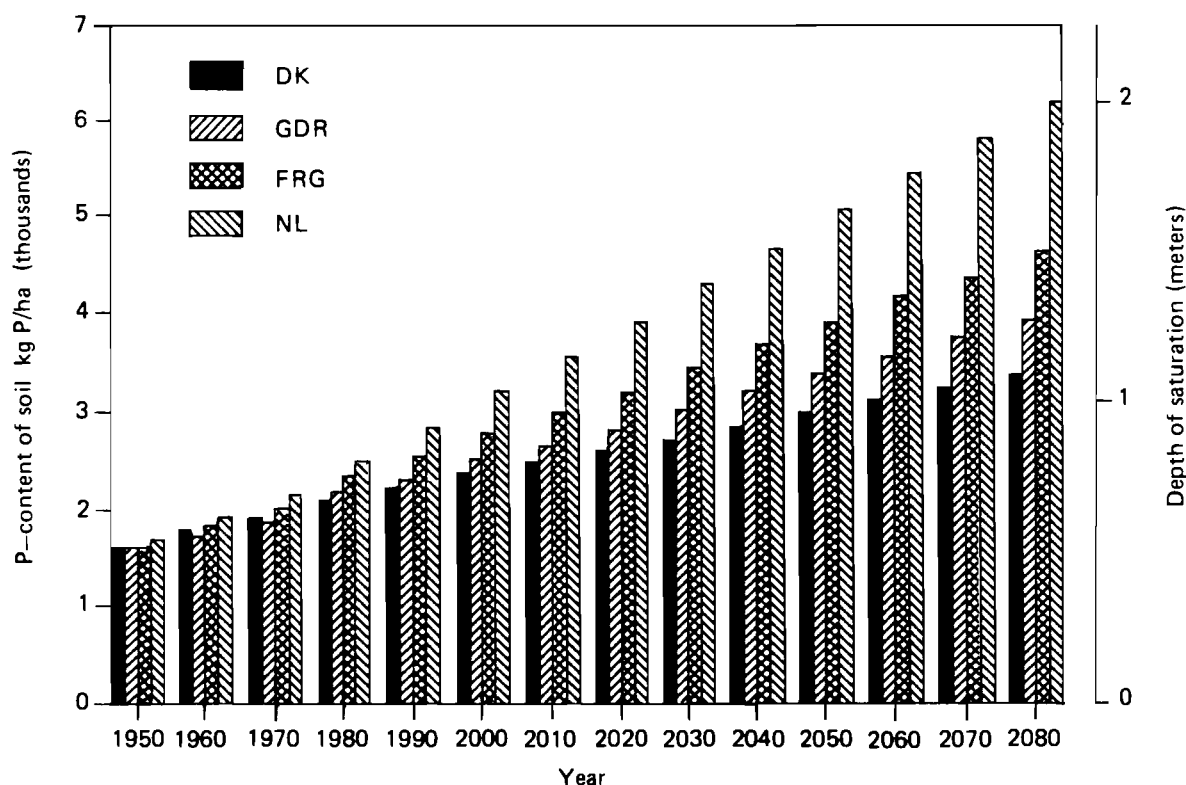
Figure 12   Projected changes of phosphorus content of soils from 1950 to 2080 in Denmark (DK), the German Democratic Republic (GDR), the Federal Republic of Germany (FRG), and the Netherlands (NL). The right-hand scale shows the depth of saturation assuming a PSC of 30 kg P/ha/cm. Estimates were based on the assumption that phosphorus application in future would be the same as for the period 1980 to 1985. Source: Behrendt, 1988.

In addition to heavy metals, certain organic pesticides also tend to accumulate in soils by a similar mechanism. Two examples are diquat and paraquat, each of which have a half-life in soils of at least 10-20 years (de Hann, 1987). As shown in Figure 13 for the case of diquat, such pesticides also contain positive charges and thus may be adsorbed at cation exchange sites.

The most important question regarding these stored toxic materials is the potential in the future for increased mobility, resulting in their leaching into groundwaters or uptake by edible plants. In order make such an assessment, it may be useful to apply the so-called "bottom-up" approach described by Parry and Carter (1987). In this method, one focusses on the potential impact, which in this case is the possible mobilization of toxic materials from agricultural soils, and asks to which factors is the impact most sensitive.

It is well known from the extensive literature on acid deposition, that acidification of soils is associated with the increased mobility of heavy metals. (For example, see Dickson, 1980, and NRC, 1985.) This is true in part because a decrease in pH results in increases in the concentration of H^+ in soil solution, as well as in increases in Fe^{+3} and Mn^{+3} which are more soluble at lower pHs. These cations compete with heavy metals (and possibly with organic pesticides such as diquat) for cation exchange sites, rendering the latter to be less adsorbed and thus more mobile.
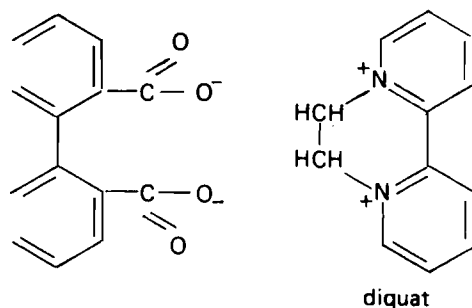
Figure 13 Schematic representation of diquat bonding on soil organic matter. Source: de Hann, 1987, and Stevenson, 1972.

The important point for the subject of this paper, however, can be observed in Figure 14. Laboratory experiments have shown that the percent of heavy metal cation adsorbed to soil components undergoes an abrupt change over a narrow pH range. Table 1 presents values of pH_{50} (the pH at which 50 % of the original cation concentration is adsorbed) for various heavy metals on two different soil substrates.
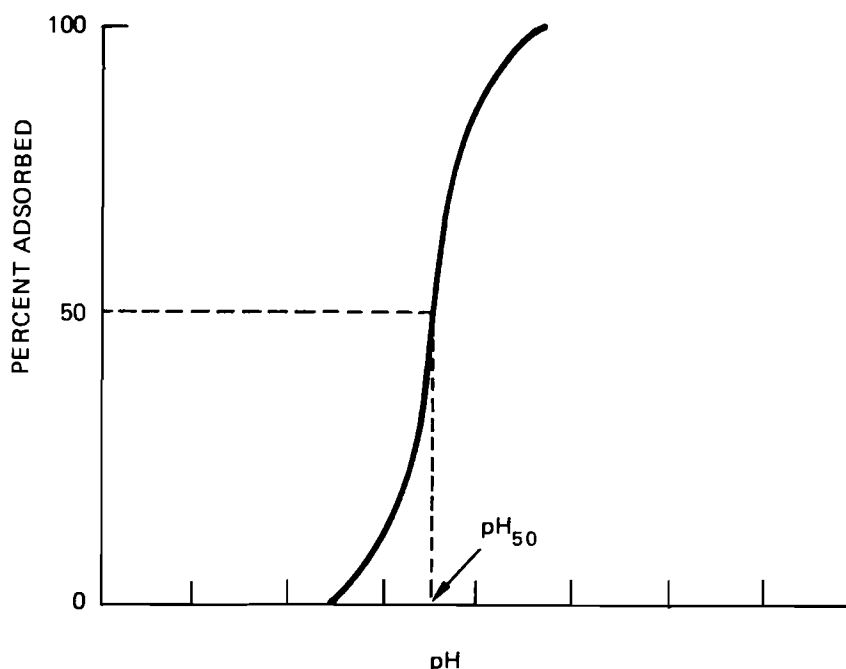
Figure 14 Typical pH adsorption curve for divalent cations on hydrous metal oxides (pH_{50}) values may range from about 3 to 8). Source: NRC, 1985.

Heavy metals commonly found in European agricultural soils include cadmium, chromium, copper, mercury, nickel, lead, and zinc (Sauerbeck, 1987). Of these, cadmium, copper, nickel and zinc are most readily mobilized under acidic conditions. Cadmium has been one of the most thoroughly studied heavy metals because of its high toxicity and high biological activity. Large quantities have inadvertently been added to agricultural soils because it occurs as an impurity in phosphate fertilizers, ranging from 5 ppm to 300 ppm depending on the source of fertilizer (Henkens, 1983). In addition, other major

Table 1. Adsorption of Trace Heavy Metals on Colloidal Metal Hydroxides

Fe $(OH)_3$ gel[a]									
metal[b]:	Pb	<	Cu	<	Zn	<	Ni	<	Cd
pH_{50}:	3.0		4.3		5.3		5.7		5.9
Al$(OH)_3$ gel									
metal:	Cu	<	Pb	<	Zn	<	Ni	<	Cd
pH_{50}:	4.8		5.2		5.6		6.3		6.6

[a]) Gel concentration: 9.3×10^{-2} M Al or Fe
[b]) Trace metal concentration: 1.25×10^{-4} M
Source: NRC, 1985.

sources of cadmium pollution include incineration of domestic and commercial wastes, application of sewage sludge to agricultural areas, combustion of fossil fuels, zinc smelting, and effluent wastes from various industrial activities. Olsthoorn and Thomas (1986), have estimated that accumulations of cadmium in Dutch soils from all sources could cause a doubling of cadmium content (to 0.6 ppm) by the year 2060.[5] Foerstner (1986) estimated a possible increase of cadmium levels to a critical 3 ppm in some Swiss soils within the next 20-30 years, if the current practice of composting cadmium-contaminated wastes is continued.

3.3. Potential Vulnerabilities in the Future

Having established soil acidification as a major determinant of the mobility of toxic materials in contaminated soils, it is necessary to review the possibilities in the future for broad-scale changes in the acid status of agricultural soils. On a regional scale, the most important source of acidity has been acid deposition from the combustion of fossil fuels. We have seen in the previous section that the forest soils of Central Europe are severely threathened by further acidification. On a more local scale, major sources have been acid drainage from coal mining activities (Brugam and Luck, 1986), and drainage, for agricultural purposes, of wetlands containing large deposits of reduced sulfur minerals (Renberg, 1986).

Until now, agricultural soils have been somewhat protected from acidification due to the routine practice of liming, which helps to maintain the soil's structural stability and raises the soil's pH to near neutral to alkaline conditions. Indeed, experiments have already demonstrated the effectiveness of decreasing the bioavailability of cadmium by raising the pH of agricultural soils. John et al. (1972) and Miller et al. (1976) found that decreasing soil pH was associated with increasing concentrations of cadmium in radish, lettuce, and soybeans. Williams and David (1976) amended a soil [pH = 5.4, <1μg Cd/g soil (1 N HCl extraction)] with $CaSO_4$ to pH 5.1 and with $CaCO_3$ or $MgCO_3$ to pH 6.0 and 6.8. They observed that the uptake of cadmium by subterranean clover increased when the pH was lowered and decreased when the pH was raised. Working with a soil amended with cadmium at varying rates (0 to 100 μg Cd/g dry soil), John (1972) found that an application of lime $(Ca(OH)_2)$ which increased the pH of the soil from 4.1 to 5.5 resulted in decreased cadmium concentrations in radish tops and roots. Other

[5]In the Netherlands soils containing 1 ppm of cadmium are considered to be contaminated.

investigators (Williams and David, 1973; MacLean, 1976; Wallace et al., 1977) have observed decreased cadmium uptake by subterranean clover, lettuce, and corn with additions of lime or $CaCO_3$ to the soil.

However, perhaps a new source of soil acidification in Europe may occur if current plans to cut back agricultural production, for example in the EC countries, are enacted. The agricultural sector in most of the countries in the EC is overproducing by approximately 20%. Serious discussions are currently underway to reduce, by a large fraction, the areas currently engaged in agricultural activities. One result may be the "abandoning" of farm land on a very large scale, perhaps 20% or more. If these lands are no longer limed, there may be a large and rapid increase in acidity of the soils followed subsequently by leaching of toxic materials.

On the other hand, recently public concern about the issue of toxic chemicals in aquatic and agricultural systems has resulted in more stringent laws within the EC and elsewhere in Europe, which may well reduce the levels of toxic materials flowing through the European environment. Such laws often set standards of maximum permissible limits for toxic materials in soils, foods, or water bodies. However, as described in the previous discussion, the underlying physical and chemical conditions of the soil are the most important factors determining the mobility of toxic materials in the environment. Thus, setting standards alone without consideration of the physical and chemical factors may not be enough to ensure that safe levels of toxic materials are maintained in the future.

In our previous discussion about sorption capacities, we stated that the ability of soils to store chemicals depends on the rate of input of the chemical and on the size of the reservoir. (See Figure 9.) In the case of abandoned lands, even though inputs of toxic materials will presumably cease, or at least be greatly reduced, materials stored from previous inputs may be released due to a rapid shrinking of the size of the reservoir. This is shown schematically in Figure 15. The effect may be aggravated if the least productive lands (the so-called "marginal" lands) are taken out of production, since these may have experienced the largest inputs of cadmium (via phosphate fertilization) and pesticides. Not much has been written about the environmental implications of abandoning agricultural land, and this topic may well merit extensive research in the future.

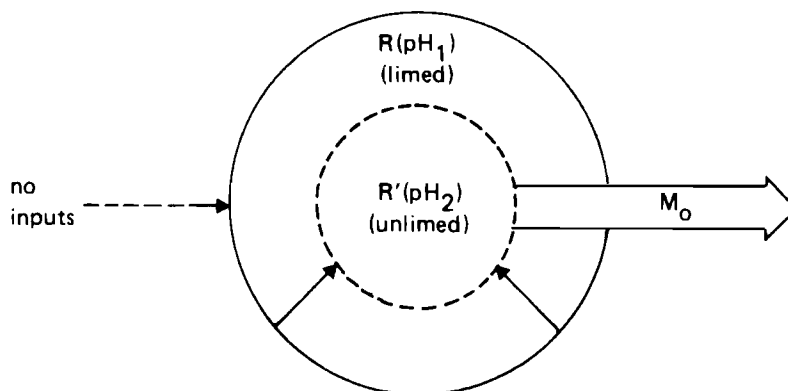Figure 15 Schematic representation of the effect of decreasing pH on the size of the reservoir for storage of toxic materials. $R(pH_1)$ is the storage capacity at pH_1, which is near neutral in limed soils. $R'(pH_2)$ is the reduced storage capacity at pH_2, which is more acidic in absence of liming.

4. OXYGEN DONATING CAPACITIES OF SOILS AND SEDIMENTS

One of the fundamental requirements of life is the need to generate biochemical energy attained through the oxidation of organic carbon to CO_2. The most efficient energy-producing mechanism is that of respiration by which molecular oxygen (O_2) is the oxidizing agent. While the atmosphere clearly possesses the most abundant source of O_2, it is not a particularly reactive medium for oxidation reactions. (This is fortuitous, for otherwise we would burn to death.) This is true because of the relatively low concentrations of chemical compounds (mostly free radicals) that are reactive enough to overcome the high energy needed for breaking the oxygen-oxygen bond of O_2. The opposite situation applies to oxidation reactions in waters and bottom sediments. Here there are plentiful microorganisms capable of utilizing O_2 in respiration, but such reactions are restricted by the relatively low solubility of O_2 in water. However, the earth's aquatic ecosystems contain abundant populations of microorganisms capable of utilizing oxygen from other oxygen-containing compounds. Generally, soils are even more reactive than water systems. They may possess a greater capacity than waters for the absorption of O_2, and they support even greater populations of microorganisms that obtain energy through respiration, or through oxidation reactions utilizing oxygen from other oxygen-bearing molecules.

Because soils, waters, and sediments are all ultimately limited with respect to the availability of O_2, invariably microorganisms appropriate the required oxygen from oxygen-bearing molecules. The following chemical sources are utilized ubiquitously in the biosphere: nitrate (NO_3^-), manganese and iron oxides (Mn_2O_3, Fe_2O_3), sulfate (SO_4^{-2}), and carbon dioxide (CO_2). However, as shown schematically in Figure 16, the extraction of oxygen from these compounds proceeds via a preordained ordering, rather than by random utilization of all available oxygen. This ordering results from the relative oxidation efficiencies of each molecule, or, in chemical terms, their "redox" potential. (When an oxygen atom is extracted, the compound donating the oxygen is "reduced", and the compound receiving the oxygen is "oxidized", hence the term "redox".) One can think of the redox potential as a kind of "chemical switch" mechanism, determining the observed sequence by which these chemicals are utilized by microorganisms.

Moreover, as described in Table 2 and elaborated upon in the following discussion, each of the redox reactions is associated with characteristic chemical by-products that may affect the environment in different ways. Sudden changes in the redox potential are possible, which may lead to deleterious environmental effects that appear as sudden, and often unpredictable, occurrences. Some examples of how this behavior may create serious environmental problems are described in the following discussion.

4.1. Anoxia in Coastal Waters

Anoxia may occur in intermediate or deep waters of a gulf or a fjord with restricted circulation with surface waters (R. Wollast, Free University of Brussels, personal communication, 1987). Figure 17 illustrates the underlying mechanism. As carbon is gradually added to the deeper waters, O_2 is progressively consumed by aerobic bacterial activity, and, since there is little mixing with the surface layers, replenishment of O_2 from the atmosphere does not occur. (The oxygen present in one liter of sea-water is sufficient to oxidize approximately 4 mg of organic carbon.) When the amount of organic carbon exceeds 4 mg/l, a sudden drop of redox potential occurs. Because sea water is rich in sulfate salts relative to other oxygen-containing compounds, the favored reaction is sulfate reduction to hydrogen sulfide (H_2S), a chemical that is extremely toxic to fish and humans. Although H_2S is generally confined to the lower layers of sea water, during a storm event, there may be rapid mixing of the deeper, anoxic layers with the surface layer, resulting in massive fish kills from exposure to H_2S.

$CH_2O + O_2 \rightarrow CO_2\uparrow + H_2O$

500

$CH_2O + NO_3^- \rightarrow N_2\uparrow + CO_2\uparrow$

Redox potential (mV)

300

$CH_2O + X-MnO_2 \rightarrow Mn^{+2} + X \text{ (mobile)} + CO_2\uparrow$

$CH_2O + X-Fe(OH)_3 \rightarrow Fe^{+2} + X \text{ (mobile)} + CO_2\uparrow$

100

$CH_2O + SO_4^{-2} \rightarrow H_2S\uparrow + CO_2\uparrow$

0

−100

$CH_2O + CO_2 \rightarrow CH_4\uparrow + CO_2\uparrow$

−300

4   8   12   16   20   24

mgC/liter
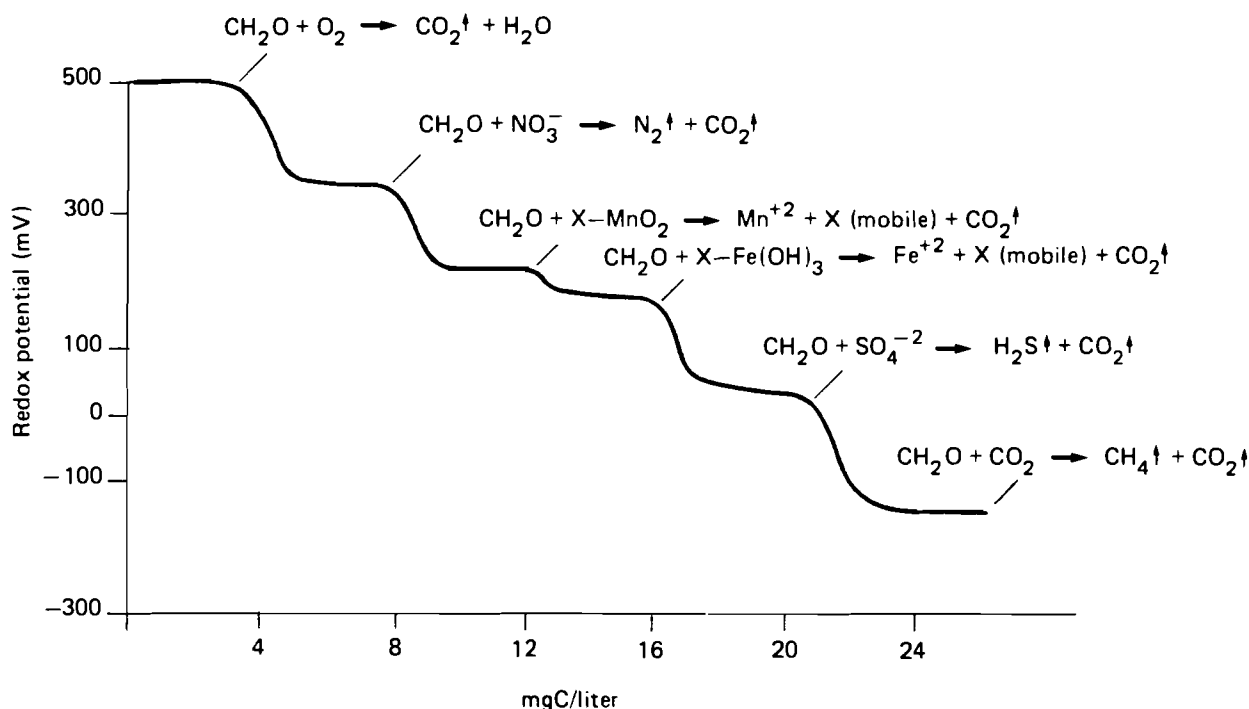
Figure 16 Schematic illustration of the order in which microorganisms select oxygen-bearing molecules for oxidation of organic carbon to CO_2 in O_2-deficient environments. O_2 in natural waters is sufficient to oxidize about 4 mg of organic carbon (CH_2O) per liter of water. When O_2 is not replenished from the atmosphere, the oxygen will be extracted from other molecules in the order shown. See Table 2 for more detailed descriptions.

As shown in Figure 18, in coastal areas of Denmark in 1981 and again in 1983, there were unprecedented depletions of oxygen and releases of hydrogen sulfide, causing the killing of large numbers of fish. The Danish National Agency for Environmental Protection concluded, in a comprehensive investigation, that meteorological conditions had triggered the two episodes, but that the underlying cause was the increasing over-fertilization of the coastal waters with an accompanying over-abundance of oxidizable organic carbon. The source of nutrient inputs was primarily nitrogen from agricultural activities (Schroder, 1985). This same phenomenon has been observed in the Gulf of Saronik near Athens. The cause in this case is not nutrient run-off from agricultural activities, but the direct disposal of sewage, again containing large concentrations of oxidizable organic carbon, from the city of Athens (R. Wollast, Free University of Brussels, personal communication, 1987).

4.2. The Impact of Dredging Sediments in Coastal Areas

4.2.1. Magnitude of the Problem

For nautical reasons, dredging of sediments in rivers, estuaries, and coastal areas, and subsequent aquatic or upland disposal of the dredge spoils are routine activities carried out all over the world. However, in the process of raising, transporting, and disposing of the sediments to new environments, sudden changes in redox potential may occur, as for example, when sediments pulled from anoxic waters are exposed to the atmosphere.

Table 2.

| REDOX REACTION	REACTION PRODUCTS/CONSEQUENCES
1. $O_2 + CH_2O \rightarrow CO_2 + H_2O$	The aerobic condition, characterized by the highest redox potential, occurring when there is an abundance of O_2, and the relative absence of organic matter owing to oxic decomposition by aerobic microorganisms prior to burial. Two examples are the aerobic digestion of sewage wastes, and the decomposition of organic matter near the surface of well aerated soils. The end products, CO_2 and water, are typically benign.
2. $(4/5)NO_3 + CH_2O + (4/5)H^+ \rightarrow CO_2 + (2/5)N_2 + (7/5)H_2O$	When molecular oxygen is depleted from the soil, as would be the case, for example, in water-logged soils, available nitrate is the most efficient source of oxygen. Denitrifying bacteria extract oxygen and release N_2 and N_2O. In agricultural soils, this process can lead to losses of nitrogen fertilizer amounting to as much as 20% of inputs (Behrendt, 1987). Denitrifying bacteria are also very active in heavily polluted rivers having long residence times, or in stratified estuaries where organic matter accumulates. In some estuary systems denitrification may significantly affect the transfer of nitrogen to the adjacent coastal waters and to the atmosphere.
3a. $2MnO_2 + CH_2O + 4H^+ \rightarrow 2Mn^{+2} + 3H_2O + CO_2$ 3b. $4Fe(OH)_3 + CH_2O + 8H^+ \rightarrow 4Fe^{+2} + 11H_2O + CO_2$	In anaerobic environments in which nitrates are in low concentration and manganese and ferric oxides are abundant, the metal oxides may be a source for microbial oxidation. This may be the case in natural soils, and in the sediments of lakes and estuaries. The environmental significance of these metal oxides is that they serve a dual role. Not only are they a source of oxygen to microorganisms, but also, they are important for their capacity to bond toxic heavy metals, deleterious organic compounds, phosphates, and gases. When the metal oxides are reduced, they become water-soluble, and lose their bonding ability. This loss may result in the release of toxic materials.
4a. $(1/2)SO_4^{-2} + CH_2O + (1/2)H^+ \rightarrow (1/2)HS^- + H_2O + CO_2$	Sulfidic conditions are brought about almost entirely by the bacterial reduction of sulfate to H_2S and HS^- accompanying organic matter decomposition. Sulfate reduction is very common in marine sediments because of the ubiquity of organic matter and the abundance of dissolved sulfate in sea water. Such reactions are also important in areas affected by acidic deposition in the form of sulfuric acid. H_2S is an extremely toxic gas. Sulfides are also important in scavenging heavy metals in bottom sediments.

4b. $MeS_2 + (7/2)O_2 + H_2O$
$\rightarrow Me^{+2} + 2SO_4^{-2} + 2H^+$
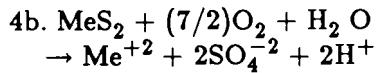
The reverse reaction, in which a heavy-metal sulfide (MeS_2) is converted to sulfate may also occur, when anaerobic sediments are exposed to the atmosphere, as in the case of the raising of dredge spoils. It may also occur when wetlands containing pyrites (FeS_2) are drained for agriculture, or in coal mining areas as acid mine drainage. One consequence may be an increase in acidification from the generation of sulfuric acid; another might be the release of toxic metals.

5. $(1/2)CO_2 + CH_2O$
$\rightarrow (1/2)CH_4 + CO_2$
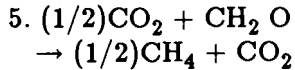
Under anaerobic conditions at a redox potential of less than -200 mV and in the presence of specialized bacteria as may be found in swamps, flooded areas, rice paddies, and the sediments of enclosed lakes and bays, oxygen may be extracted from CO_2 with the emission of methane. This reaction is more typical in freshwater systems because sulfate concentrations are much lower than in marine environments, averaging about one-hundreth the concentration in seawater. Methane is a critical gas in the determination of global climate. Since the early 1970s, global atmospheric methane levels have been increasing at a rate of 1% per year. Although the reasons for this increase are still under investigation, the expansion of rice paddy cultivation in southeast Asia has been cited as a likely explanation (Crutzen and Graedel, 1986).

In industrialized countries, such sediments are usually highly contaminated with toxic heavy metals, pesticides, and other industrial pollutants. Whereas these chemicals may be relatively immobile under the redox conditions of the under water environment, a change in redox conditions may render them much more available for biological up-take with serious environmental consequences.

It should be noted that the great rivers flowing through industrialized countries of Europe, North America, eastern Asia, and elsewhere are the recipient of enormous quantities of toxic materials generated from industrial and agricultural activities conducted within their drainage basins. While great quantities of these materials are deposited in the rivers' sediments, huge amounts are also transported to the estuaries and the costal zones at the rivers' mouths. Although spectacular industrial accidents causing a large pulse of polluting chemicals to enter the river (but with short-lived effects) often are the focus of attention in the media, the problem of toxic materials accumulating year by year in the water courses and coastal areas may be far more serious. For example, in a well-publicized industrial accident on the Rhine River at Basel in November, 1986, 33 tons of toxic chemicals were released to the river. In comparison, the annual discharge of the Rhine into the North Sea contains more than 10,000 tons of toxic chemicals, and the total quantity of chemicals released from the single accident was about equal to one day's normal discharge of chemicals at the river's mouth (Clark, 1986a). When viewed over many decades, the problem becomes more critical, for these great rivers have effectively transported hundreds of thousands of tons of toxic materials downstream and into the estuaries and coastal zones. As shown in Figure 19, evidence from sediment cores taken from coastal waters of the North and Baltic Seas indicate that toxic heavy metals have been accumulating for well over 100 years.
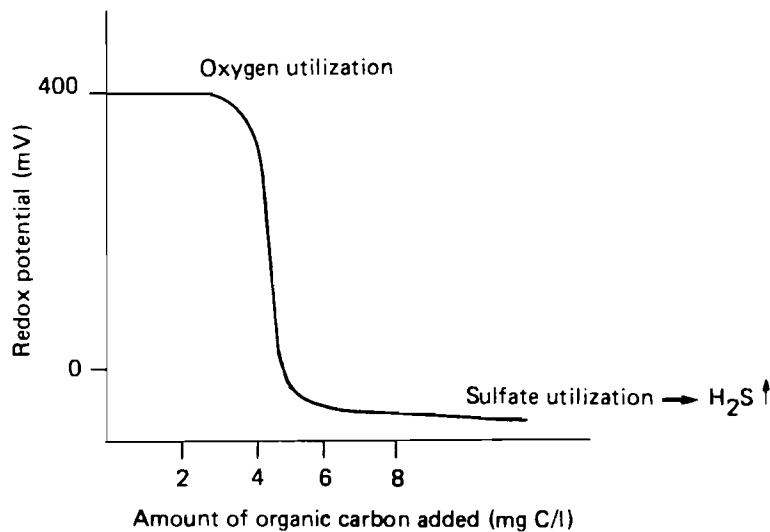
Figure 17 Mechanism for production of toxic H_2S in marine waters with an abundance of organic carbon, and restricted circulation of surface waters. Because of the relative abundance of sulfates in marine waters with respect to other oxygen-bearing molecules, reduction of sulfate is the dominant reaction under anaerobic conditions.

One of the most polluted of all regions is the Delta area in the Netherlands, where not only the Rhine, but also the Scheldt and the Meuse empty into the North Sea. To keep navigation lanes open in the Nieuwe Waterweg and adjacent ports of Rotterdam, about 50,000,000 tons (approx. 20,000,000 cu. meters) of spoil are dredged annually (V&W, 1987). Table 3 shows the concentrations of eight heavy metals in the sediments of the Scheldt and Rhine estuaries in the 1970s. To place these values in perspective, the Dutch government in 1983 established some concentration standards for defining contaminated soils. For heavy metals these were soils with concentrations higher than the following: arsenic (20 ppm), cadmium (1 ppm), chromium (100 ppm), copper (50 ppm), lead (50 ppm), mercury (0.5 ppm), nickel (50 ppm), and zinc (200 ppm) (VROM, 1980). Formerly, the dredge spoil was used to fill polder land in the Netherlands. However, as one may observe in Table 4, this practice polluted the land so badly that such deposits are now forbidden by law. Currently, dredge spoils of the Dutch coastal areas are a massive solid waste problem that remain unsolved to this day.

4.2.2. Changes in Redox Potential as a Major Source of Release of Toxic Materials from Dredge Spoils

In sulfate-rich estuarine and marine ecosystems under anaerobic conditions, toxic heavy metals are often trapped in sediments as insoluble sulfides and organically bound species, forms that are relatively immobile and not readily available for bioaccumulation. The anaerobic condition may be maintained by the excessive quantities of organic carbon and nutrients often found in these waters, the result of upstream inputs from industrial and agricultural activities and domestic sewage. Thus, the sediments of highly polluted coastal areas fed by major water courses such as the Rhine serve as vast depositories for accumulated toxic wastes, often present in an environment that generally suppresses their toxicity. However, as shown in Figure 20, under certain changing physiochemical conditions accompanied by mechanical disturbance, the sediments can be a *source* of release of these chemicals, rather than a *sink* for their retention.
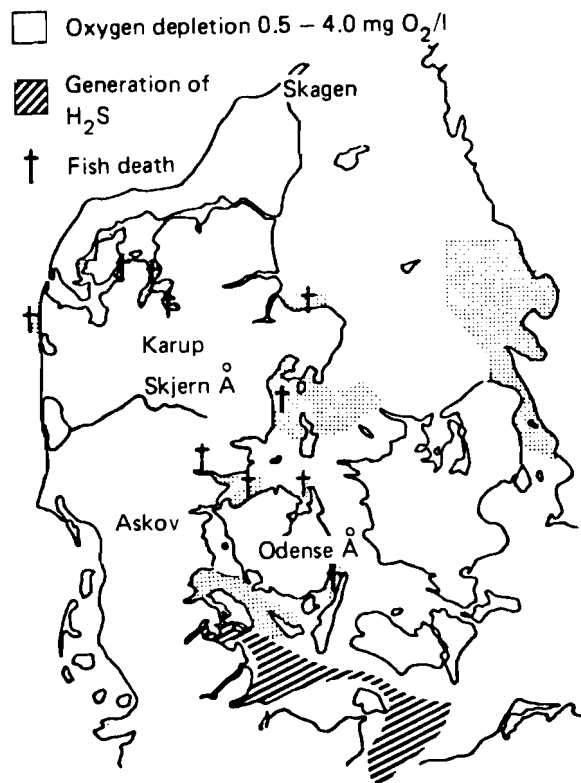
Figure 18　　Coastal areas in which oxygen depletion, fish suffocation, and generation of $H_2 S$ were recorded in September 1981. Source: Miljostyrelsen, 1984.

As noted by Foerstner (1986), the remobilization of heavy metals from sediments can be increased by four factors: (1) changing the redox conditions; (2) lowering the pH; (3) increasing the salt concentration; and (4) increasing the occurrence of natural and synthetic complexing agents which can form soluble metal complexes. Furthermore, mechanical perturbation (erosion, dredging, bioturbation) can also affect remobilization of metals. In our discussion we will mainly focus on factors 1 and 2. It is important to mention however, that factor 3 may play an important determining role when, for example, harbor sludge from inland areas is dumped into outer, more saline estuary areas. This method of disposal may increase considerably in the future as national governments regulate more stringently, the option of deposition in land-fill areas (Prause et al., 1985). Figure 21 shows the remobilization of cadmium from contaminated sediments in the Weser River near Bremen upon exposure to estuarine conditions. The remobilization mechanism appears to be metal-specific, however, since lead, which is characterized by its high affinity to particle surfaces, exhibits no tendency for remobilization. It was suggested by Prause et al. that in the river sludge, cadmium was bound to the SH-group of organic material. Upon dumping in the outer estuary, this bonding position was broken as bacterial activity oxidized the SH-group to sulfate during the decomposition of the organic matter. So apparently, even the observed effect of increased remobilization with increasing salinity may be intricately linked to changes in redox potential. (See also Compeau and Bartha, 1984 who postulate an inverse correlation of salinity with mercury methylation due to the reduction, in low-redox-potential marine environments, of sulfate to $H_2 S$, an inhibitor of methylation.)

GERMAN BIGHT (North Sea)   KIELER BUCHT (Baltic Sea)
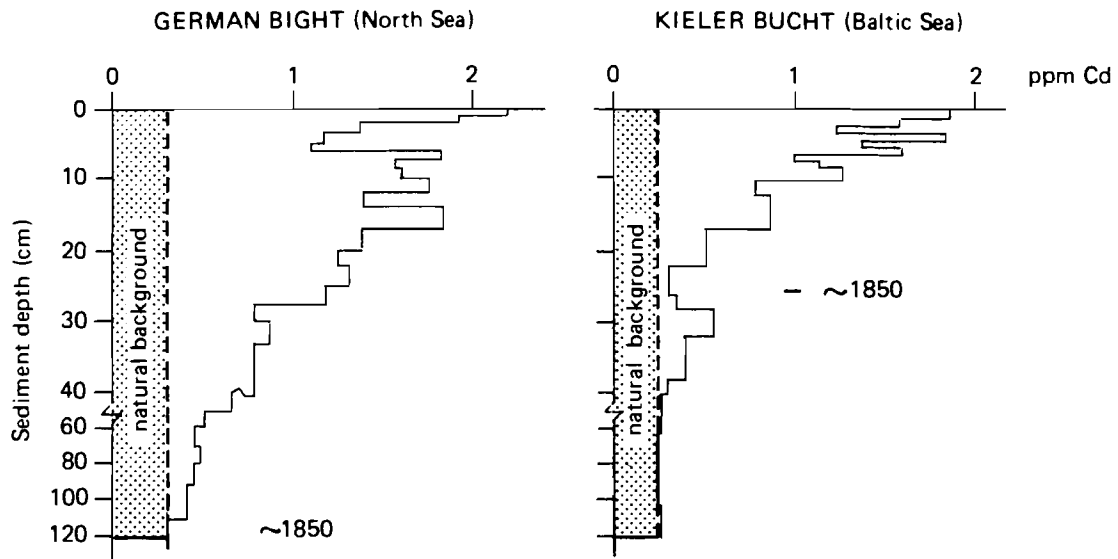
Figure 19   Chronological development of cadmium concentration in the North Sea and Baltic Sea as derived from analyses of sediment cores from the German Bight and Kieler Bucht. Source: Foerstner, 1980 and references cited therein.

Table 3. Metals in the Sediments of the Scheldt and Rhine Estuaries

(mg per kg dry matter)	Ars-enic	Cad-mium	Chro-mium	Cop-per	Merc-ury	Lead	Nickel	Zinc
Antwerp								
1974	84	37	510	200	3.8	260	71	1,500
1979	94	35	290	180	3.0	260	60	990
Vissingen								
1974	18	1.2	100	29	0.7	65	24	180
1979	21	2.0	100	28	0.5	46	26	170
Rijn-, Mass- and Waal ports								
1977	-	26	480	230	5.6	310	60	1,400
1979	33	27	480	210	4.2	310	62	1,500
Europoort								
1977	-	3.2	130	42	1.0	81	25	290
1979	18	3.7	150	38	0.9	80	27	310

Sources: IB, 1987a, WL, 1987.

Table 4. Metals and Organochloro Compounds in the Soils of Polders Raised with Dredging Spoil from Rotterdam Ports, 1973-1978

	Broekpolder			Buiten- Nieuwlandse Polder	Delfland Polder
	median	minimum	maximum (mg per kg dry matter)	median	median
Arsenic	55	35	65	70	59
Cadmium	9.2	5.5	18.8	6.9	6.4
Chromium	238	178	396	230	213
Copper	139	93	186	138	127
Mercury	4.5	3.2	6.5	4.8	4.2
Lead	211	156	292	220	206
Nickel	43	39	51	43	40
Zinc	808	580	1,154	808	729
HCB	0.11	0.02	0.39	1.03	0.05
Drins	0.50	0.03	66	0.02	1.61
PCBs	1.33	0.62	2.05	1.09	0.63

Source: IB, 1987b.
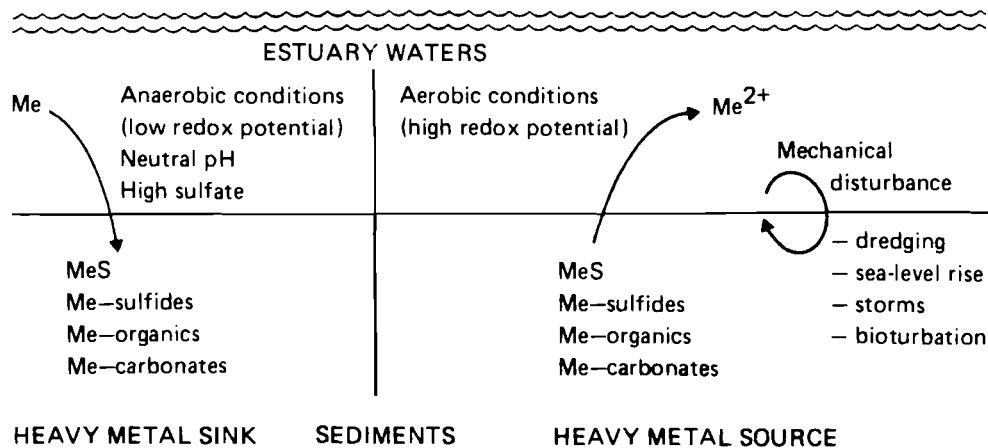
Figure 20   Estuarine sediments as a sink and a source of pollution by heavy metals, (Me).

Mobilization via factor 4 will not be discussed in detail. There have been some studies suggesting that complexing agents have increased the mobility of heavy metals in some cases. The most well-known example is that of nitrilotriacetate (NTA), a substitute for polyphosphates in detergents. Several studies have demonstrated the effect of NTA on the remobilization of metals from sediments (Salomons and Van Pagee, 1981; Salomons, 1983).
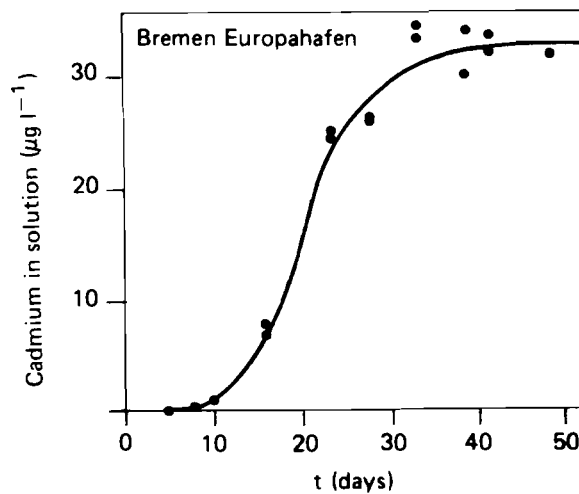
Figure 21   Remobilization of cadmium as a function of time upon exposing harbor sludge to saline conditions typical of outer-estuarine areas. The sludge is from the Europahafen Bremen, resuspended in seawater 32 /oo; pH = 7.9; temp. = 7 ° C; O_2 = 9 mg/l; 10 g solids/l. Source: Prause et al., 1985.

The influence of pH and redox potential on the biological availability of heavy metals is exemplified for the case of cadmium in Figure 22. One may observe that under oxidized conditions at pH values less than 7, the cadmium is mostly available in water-soluble form (Cd^{+2}). At pHs of about 8 and higher, cadmium concentration is governed by the solid phase ($CaCO_3$), which is biologically unavailable. At very high values of pH (10 or greater which is not very common in natural systems) soluble forms of cadmium again predominate. On the other hand, under reducing conditions (Eh < 0) cadmium is present predominantly as the insoluble sulfide. As described previously, such would be the typical case in anoxic marine sediments. In natural environments the chemistry of cadmium is more complex than depicted in Figure 22. The metal may exist not only as precipitated sulfide, but also in other solid phases as well; e.g., as precipitated organically-bound species, or on adsorption sites of hydrous metal oxides. Nevertheless, the overall effect of exposing these sediments to the atmosphere is a large increase in the potential mobility of these metals;
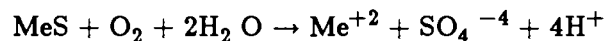
$$MeS + O_2 + 2H_2 O \rightarrow Me^{+2} + SO_4{}^{-4} + 4H^+$$

(See also Table 2, reaction 4b)

As shown in the above reaction, the oxidation may also be accompanied by an increase in acidity (H^+). Referring again to Figure 22, one may observe that an increase in both acidity and in redox potential greatly favors the soluble form of cadmium.

Indeed, greatly increased mobility of cadmium and increased acidity have been observed in field studies when near-neutral pH, noncalcareous, dredged sediments high in sulfide and organic matter were exposed to oxidized conditions at upland disposal cites (Gambrell et al., 1977; Khalid, 1980). De Groot (1977) studied the uptake of cadmium by several agricultural crops from highly polluted Rotterdam Harbor sediments dumped at upland sites. The crops grown on dredged sediments showed a significantly higher content of cadmium than the crops grown on natural river clays. An exponential increase in cadmium uptake was observed with increasing concentrations of the element, especially in leafy vegetable and rootlike crops including lettuce, radishes, potatoes, and carrots. More recently, Kersten and Foerstner (1987) have obtained similar results.
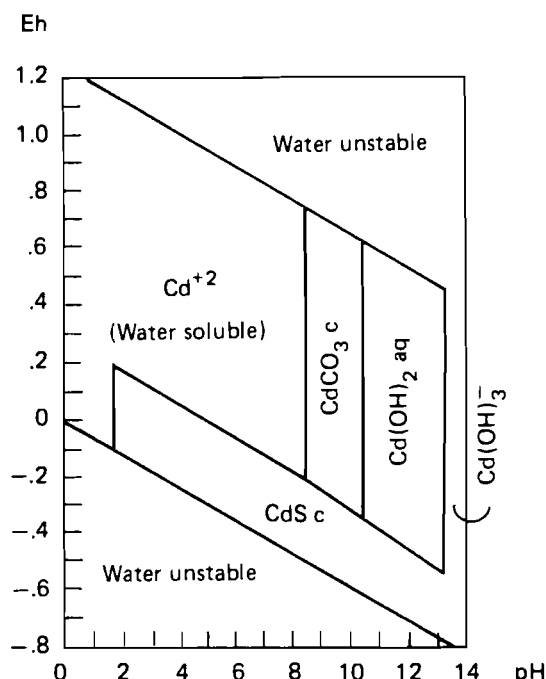
Figure 22   Fields of stability of solids (signified by c) and predominant dissolved cadmium species in system $Cd + CO_2 + S + H_2 O$ at 25°C and 1 atm in relation to redox potential (Eh) and pH. Dissolved cadmium activity, $10^{-7.05}$ mol/l; dissolved CO_2 and S species, 10^{-3} mol/l. Source: Hem, 1972.

Gambrell et al. (1980) studied the chemical availability of mercury, lead, and zinc in Mobile Bay (USA) sediment under varying pH and redox conditions. They established that the biological availability of these metals was dependent on pH and redox conditions. They further noted, however, that when the transit time between dredging and disposal was short, there would be little opportunity for the reduced, bulk solid material to oxidize before settling to the bottom of a disposal site. So over the short term there might be little observable effect. The real concern, however, is the possible releases of toxic metals caused by long-term alterations in the physiochemical environment of the designated disposal site. They recommended, therefore, that in selecting a disposal alternative, information on the potential for such long-term physiochemical changes should be factored into the management strategy.

A similar concern was raised by Berman and Bartha (1986), in a study of mercury polluted sediments in an estuarine creek in New Jersey, USA. They noted that the mercury under the prevailing conditions (pH = 6.8, Eh = -230 mV) and high sulfide environment would remain relatively immobile and harmless to biota. However, they cautioned that if ever there is a "cleanup of the contaminated sediments by dredging, it will be critical to minimize any air exposure and weathering of the dredge spoils. A speedy entombment of the Hg-contaminated dredge spoils in an anoxic sulfide-rich state, with provisions for permanent exclusion of oxygen and oxygenated ground water appears to be a long-range disposal option".

Interestingly, in the same paper, Berman and Bartha reflect briefly upon two plausible events, by which the immobile, sulfur-bound mercury could be transformed into the highly toxic and bioavailable methlylated species. One is the possibility of a storm flood that might transport some of the contaminated sediment to other areas of the estuary more conducive to the production of methyl mercury; i.e., conditions of lower pH and/or

higher redox potential.[6] The other possibility is, paradoxically, an improvement in the water quality due to sewage diversion that might lead to lower sulfide concentrations (and higher redox potentials), and hence a subsequent increase in Hg methylation activity.

4.3. Potential Vulnerabilities in the Future

Thus far in this section, we have established that the mobilities of toxic metals are highly dependent on changes in redox potential, pH, and to some degree salinity. The physiochemical conditions in which sediments tend to serve as sinks for toxic heavy metals are low redox potential (anoxic conditions), near-neutral pH, and low salinity. The sediments can suddenly become a source of toxic metals when the opposite conditions prevail; i.e., increases in redox potential, decreases in pH and increases in salinity.

Using again the "bottom-up approach" described earlier, it may now be useful to imagine how some of the determining factors described here could be influenced by future activities. Since the question of future possibilities for increased acidity was treated in previous sections, we will not dwell on it here. Moreover, acidification of estuarine and marine areas is not likely to occur. However, acidification may be an important factor in upland disposal sites; i.e., if such sites continue to acidify in the future, increased leaching of toxic materials may occur.

With regard to broad scale changes in redox potential, we may again recall Berman and Bartha's rather paradoxical idea about an increased risk of mercury mobilization in the event of a clean-up of sewage emptying into the estuary. On the other hand, this is not so paradoxical if we recall that the effect of sewage wastes in water bodies is to reduce the redox potential and to foster anoxic conditions, which are precisely the conditions that suppress the mobilization of heavy metals.

We have seen that the great rivers, estuaries, and coastal areas of Europe are now unwittingly huge toxic waste dumps. What will be the effect on these contaminated sediments, if there is an improvement in water quality, through stricter regulations for the discharge of sewage wastes, and reductions in runoff of nitrogen fertilizers to these water bodies? Many nations in Western Europe are already moving in those directions. If, as mentioned previously, agricultural activity is reduced by at least 20%, there could be even larger decreases in discharge of nitrate.

A few laboratory studies have been conducted in order to ascertain the effects of the relaxation of pollution pressure on heavily contaminated sediments. As shown in Figure 23, Chen et al., 1976 and Lu and Chen (1977) demonstrated that such sediments release metals when maintained under oxidizing conditions. Hunt and Smith (1983) studied the fluxes of remobilization of copper, lead, iron, manganese, and cadmium from sediments in highly polluted Narragansett Bay (Rhode Island, USA). They isolated representative samples of these sediments from heavy metal inputs, and examined them under organic loading factors reduced by 60% relative to current loading. They concluded that there was a tendency for the polluted sediments to purge themselves. They also demonstrated that the so-called "bleeding" of toxic metals from the sediments under the conditions of improved water quality, generally occurred at rates considerably lower than were the current inputs to the sediments. The results are shown in Table 5. Nevertheless, one may observe that the rate of cadmium remobilization was calculated to be a not-insignificant 15% of the current cadmium inputs. One should also consider that under the

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[6] Berman and Bartha concluded that the high levels of sulfide (S^-) inhibited methyl-mercury formation. This is so because the equilibrium constant (K_s) for the reaction, $Hg^{+2} + S^{-2} \rightarrow HgS(s)$ is 10^{-52}. This very low value means that in the presence of sulfide, essentially all of the Hg will appear as $HgS(s)$. However, the activity of S can be decreased, and that of Hg increased, by lowering the pH and/or increasing the redox potential. For details, see Wood (1980), and Bjornberg et al. (1988).

physiochemical conditions of the highly polluted Bay, the sediments are a sink for these metal inputs, and under these conditions their potential toxicity is highly suppressed. The remobilized cadmium, however, under conditions of improved water quality would be much more readily available for biological uptake. Another conclusion drawn from this study was that, at least for some of the metals, the purging time (for the top 10 cm of sediment) was on the order of centuries. (For example, about 400 years for copper.)
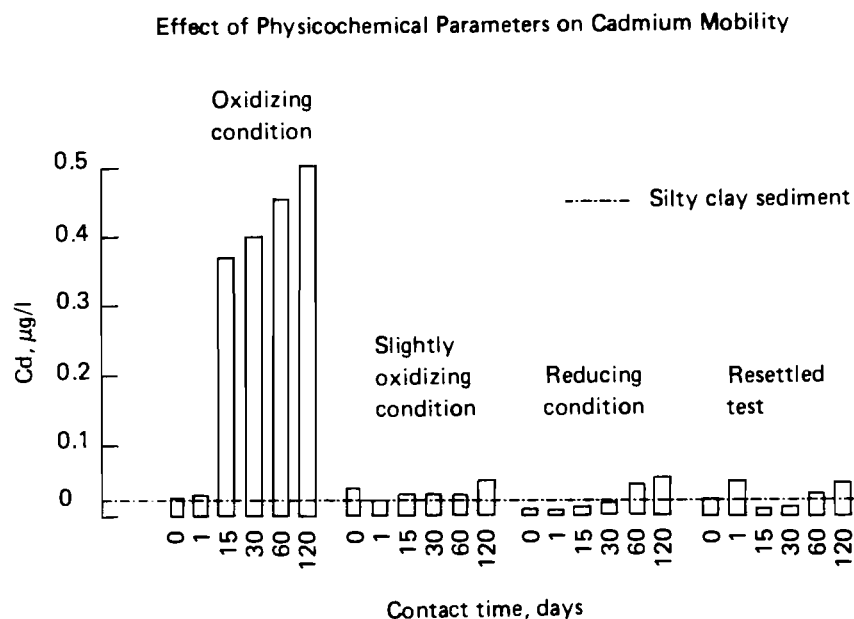
Figure 23   The effect of various oxidation-reduction conditions on the transport of cadmium in sediment-seawater interfaces in a silty clay sediment. Source: Chen et al., 1976.

Another important consideration about potential problems in the future regards the impact of climatic change (from increasing levels of CO_2 and other greenhouse gases) on the contaminated sediments, particularly the possibility of increased coastal storm events, and the potential effects of sea level rise. Climatologists generally agree that there will be an increase in the frequencey of extreme events, and presumably this means storm events as well. Will more frequent sea storm surges increase the stirring up of the sediments; perhaps moving them to new environments more conducive to remobilization, or mixing them with more oxygenated surface waters? And what would be the effect, say, of an 80 cm sea level rise on the coastal and estuarine sediments? Will the encroaching seas further stir up and transport the sediments so as to render them more mobilizable? Will there be increased salinity in the inland reaches of the estuary systems, and will this increase lead to increased mobilization? These may be important questions that deserve answers well before such events are upon us.

Table 5. Comparison of the Daily Input of Cu, Pb, and Cd to Naragansett Bay with the Calculated Output from Remobilization Under Conditions of Improved Water Quality

Metal	Current Inputs to Bay $(\text{mol} \times \text{d}^{-1})^b$	Remobilized from Sediment[a]	
		Providence River $(\text{mol} \times \text{d}^{-1})^b$	Upper Bay $(\text{mol} \times \text{d}^{-1})^b$
Cd	48	2	5
Cu	3000	46	100
Pb	780	1	2.5

[a] Under conditions of improved water quality.

[b] The term in parentheses signifies "moles per day". A "mole" is an "atomic-weight" number of grams. Thus 1 mole of cadmium weighs 112 grams, since 112 is the atomic weight of cadmium.

Source: Hunt and Smith, 1983.

5. OVERVIEW: DEVELOPMENT/ENVIRONMENT INTERACTIONS AND THE POTENTIAL FOR SURPRISES

5.1. Introduction

In order to plan an effective strategy for managing long-term environmental changes, including a means for anticipating "surprises",[7] it is necessary to understand the interactions that define the relationships between development activities and the environment. As discussed by Clark (1986b), it is rare that one human activity affects just one aspect of the environment. Also, conversely, it is rare that one environmental problem is caused solely by just one kind of human activity. Instead, in most cases the development activities are linked to environmental transformations in rather complicated ways. Understanding the intricacies of these linkages is what Clark has defined as a "synoptic" vision. One of the great problems in environmental management is the question of how to synthesize the substantial, yet imperfect, knowledge already gleaned from ongoing research on the biosphere, in a way that will be usable for the long-term, strategic management of the environment. One method, described by Clark (1986b) and Crutzen and Graedel (1986), employs a two dimensional matrix that identifies the sources (causes) of environmental change on one axis (including natural sources), and a small set of "critical environmental indicators"[8] (CEIs) on the other axis. Such indicators may be viewed simply as attributes of the environment that some party to the assessment believes to be important. This approach is attractive for two reasons: 1) it incorporates the synoptic approach to complex inter-relationships between economic development and environmental change; and 2) by condensing down the number of indicators to a definite, and preferably small set, it makes such an analysis "doable."

The success of this approach of course depends on choosing a set of CEIs that will serve the goals of the assessment well. In addition, it is also necessary, to the extent possible, to identify not only the primary linkages between development activities and environmental transformations (represented as changes in the CEIs), but also to identify secondary linkages. That is to say, a specific development activity A may affect a given critical environmental indicator through an intermediate influence on indicator B. In my view one of the major clues to anticipating "surprise" environmental changes is a deeper understanding of second order interactions. For it is often these interactions that camouflage the linkages between primary causes and environmental effects.

In this section we will adopt the suggested matrix approach described above. Human activities are defined in four general areas: energy use, agricultural activities, industrial activities, and commercial and domestic activities. Our CEIs will be the three "capacities" presented in the previous sections, plus "toxic chemicals accumulation", which is of course related to the other three CEIs, but is of such interest that it is highlighted here as an additional indicator. We first describe the primary interactions, as presented in Table 6, then the secondary interactions shown in Table 7, and finally a combined table (Table 8) which describes both primary and secondary interactions. Since many of the topics have been discussed at length in earlier sections of this paper, their descriptions here will be brief, and you may refer back to the relevant sections for more details.

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[7] We define surprise here as an ecological change that may occur over a period of time that is short relative to the response time required for implementing mitigation strategies.

[8] Clark (1986b) actually described what I call critical environmental indicators as "valued environmental components". I prefer my definition in the context of this paper for simple semantic reasons. One of my CEIs, "Toxic materials accumulation", is hardly a "valued" component.

5.2. Primary Interactions: Table 6

Interactions from Energy Use (Boxes 1 and 4)

Moving horizontally across Table 6, one may observe that energy production (in this case the burning of fossil fuels) causes a depletion of buffering capacities in soils through acid deposition. Also, fossil fuels contain trace quantities of heavy metals which are volatilized during combustion, transported through the atmosphere, and deposited in the environment. Another toxic by-product of combustion is the formation of a class of organic chemicals named polynuclear aromatic hydrocarbons (PAHs). These are distributed in the environment by a mechanism similar to that of toxic heavy metals.

Interactions from Agricultural Activities (Boxes 5-8)

Buffering capacities of agricultural soils are maintained by the application of lime $Ca(OH)_2$. Approximately 50% of European land is used for agriculture, and a large fraction of this land is regularly limed. In contrast to acid deposition, liming replenishes, rather than depletes agricultural soils. The effects of acid deposition have already affected the amounts of lime applied in the most acid-sensitive soils. For example, Swedish farmers, at a significant cost, have increased application rates in recent years to offset the effects of acid deposition (R. Wright, Norwegian Institute for Water Research, Oslo, personal communication, 1988).

Application of phosphate fertilizer has led to the accumulation of phosphorus in soils, resulting in depletion of the phosphorus sorption capacity. Also, some heavy metals and certain pesticides have accumulated in agricultural soils. Cadmium, present as an impurity of phosphate fertilizers, is applied inadvertently during fertilizer application. The same is true of other toxic metals from contaminated manure and sewage sludges used as fertilizers.

Agricultural activities also greatly affect the redox potential of water bodies, mainly through runoff and leaching of nitrate fertilizer. Currently, levels of nitrates in river waters emptying into the North Sea are as much as 30 to 40 times higher than background levels (Wollast, 1983). The nutrient-rich waters support a high degree of biological productivity. As described earlier, such conditions rapidly lead to anoxia and lowered redox potential.

Agriculture also directly contributes to the accumulation of toxic materials in the environment. In addition to accumulation in agricultural soils (described in box 6), runoff of pesticides into water courses, or their seepage into groundwaters has occurred.

Interactions from Industrial Activities (Boxes 11 and 12)

Industry and manufacturing produce high volumes of carbon-containing wastes that place a high oxygen demand on receiving waters, thus affecting the redox potential of these waters. (An index of this demand is COD = carbon oxygen demand.) Major sources of pollution are manufacturers of food (animal products) and beverages, tobacco products, the chemical industry, and paper and board mills. Industrial and manufacturing wastes are responsible for about half of the total COD in European water systems; domestic sewage provides the other half. In heavily polluted rivers like the Scheldt, long stretches (tens of km) have been known to become completely anoxic. Under these conditions, organic carbon accumulates and is transported in dissolved or particulate form to the estuaries and coastal regions. The increased flow of carbon with high COD rapidly leads to anoxic conditions in these regions as well.

Industrial activities also generate large quantities of toxic wastes. These may be stored in land fills, or directly discharged to the air or water. Heavy metals are generated in the electroplating and metal-finishing industries, scrap metal recycling, the smelting of metal ores, and fossil fuel refining. Main sources of toxic organic wastes are the chemical and petrochemical industries.

Table 6. Development/Environment Interactions
       Primary Interactions

Sources \ Consequences	Buffering Capacity	Sorption Capacity (Agricultural Soils)	Redox Potential	Toxic Materials Accumulation
Energy Use	1 Acid deposition	2	3	4 Heavy metals PAHs
Agricultural Activities	5 Liming	6 Phosphate application; cadmium, other heavy metals, pesticides	7 Over-Fertilization by nitrate, subsequent discharge to water	8 Pesticide runoff
Industrial Activities	9	10	11 Discharge to water of organic carbon chemicals with high COD	12 Heavy metals; toxic organic chemicals
Commercial and Domestic Activities	13	14	15 Discharge to water of organic carbon chemicals with high COD	16 Heavy metals; toxic organic chemicals

Interactions from Commercial and Domestic Activities (Boxes 15 and 16)

A major source of environmental pollution also results from the day-to-day activities of human settlement, including work activities in the non-industrial sectors. The worse pollution is generated in large urban areas. One age-old problem has been the disposal of domestic and commercial sewage to water bodies. Untreated or partially treated sewage have high values of COD, and are a major cause of anoxia and low redox conditions in water courses.

Also there are many sources of toxic materials associated with domestic/commercial activities. A recent study in the U.S. of the toxic content of domestic garbage, estimated that the average household discarded approximately 55 to 60 g of hazardous waste per week. That amounts to about 642 metric tons of hazardous waste discarded per year for a city the size of New Orleans (population, about 600,000, Chemical and Engineering News, 1987). Burning of refuse may release some of these materials to the atmosphere, and may even create new toxic chemicals, as for example during the burning of plastics. Some of the refuse is buried in land fills, which may lead to eventual release through leaching.

Other sources of toxic materials may be released during the dissipative end uses of some consumer products. For example, asbestos-containing brakes emit asbestos in the process of braking, lead is released to the atmosphere during the combustion of leaded gasoline, and organic solvents are released to the atmosphere in the processes of painting and dry-cleaning. The day-to-day corrosion of urban structures may also be important, causing the release of heavy metals such as Zn, Fe, Cu, and Pb.

5.3. Secondary Interactions: Table 7

Buffering Capacity/Sorption Capacity (Box 3)

In the previous discussion, we explored the linkage between buffering capacity and sorption capacity in agricultural soils. We described how the buffering capacity, maintained by continual liming, generally serves to extend the soil's ability to adsorb toxic materials, and how conversely, the cessation of liming might result in the release of toxic materials, through a diminished sorption capacity.

Buffering Capacity/Toxic Materials Accumulation (Box 4)

Many examples from the literature on acid deposition demonstrate the effect of greatly increased leaching of toxic heavy metals from terrestrial ecosystems as soils acidify. Metals with the highest potential mobility in acidified soils are aluminum, cadmium, manganese, and zinc. Copper and nickel are also also mobilized but not as readily as the first set (NRC, 1985).

Redox Potential (Soils)/Buffering Capacity (Box 5)

A good example of this linkage may be found in the record of acidification of Lake Blamissusjon in Northern Sweden (Renberg, 1986). Currently, the pH of this lake is about 3, and it has been called "the most acidic lake in Sweden", even though its acidification was certainly not caused by acid deposition. The lake is situated in a coastal area near the Bothinian Bay. The water surface lies only 1 to 2 m above the present day sea level, which, with an isostatic land rise in the area of about 0.9 cm per year, means that the lake probably was isolated from the sea just two to three hundred years ago. Because the present-day watershed was previously under the sea, the soils were rich in reduced sulfide minerals. Until the beginning of this century the pH of the lake was probably 5.5 or higher. This condition prevailed as long as the watershed soils remained water-logged. But in this century, first around 1900, and then more extensively in the 1940s, the land was drained for agricultural purposes. These actions lowered the water-table of the watershed soils, thus exposing the sulfide minerals to oxidation. (See Table 2, reaction 4b for more details.) Sulfide was oxidized to sulfuric acid, causing an extreme acidification of the soils, and subsequently of the lake. There has been no recovery of the pH levels in the lake, even though agricultural activities ceased by the end of the 1960s.

Redox Potential (Soils)/Redox Potential (Waters) (Box 6)

We have seen that under anaerobic conditions in the presence of abundant nitrates and organic carbon, bacterial decomposition of the carbon will occur via the reduction of nitrate to N_2. (See Table 2, reaction 2.) One may view such a system as a nitrate trap, since the nitrate is vented to the atmosphere as N_2. This system occurs, for example, when nitrate-rich waters pass through water-logged soils rich in organic carbon. In certain situations where high concentrations of nitrate are a potential problem, this system may have a beneficial function, serving to deplete nitrate from the polluted waters.

In a rich agricultural region in the Garonne Valley in southern France, Pinay and DeCamps (1988) have investigated the role of a partially submerged riparian woods as a buffer zone for the lateral transfer of nitrates from polluted groundwaters to the River Louge. They demonstrated that a flow of groundwater through about 30 meters of the submerged soil of the woods was sufficient to remove all the nitrate. They thus demonstrated in a larger sense the effectiveness of riparian wetland zones in protecting rivers from large inputs of nitrates caused by over-fertilization of agricultural lands in the drainage basin.

The authors also described three development activities that could diminish the protective ability of these zones: 1) river regulation to prevent flooding by isolating the river bed from its floodplain. This impoundment would reduce the water-logged area all along the stretch of the river; 2) land drainage that would lower the water table and reduce the

Table 7. Development/Environment Interactions
Secondary Interactions

Consequences Sources	Buffering Capacity	Redox Potential	Sorption Capacity (Agricultural Soils)	Toxic Materials Accumulation
Buffering Capacity	1	2	3 Liming resulting in augmented sorption capacities for heavy metals, pesticides, cessation of liming resulting in diminished sorption capacities	4 Diminished buffering capacity from acid deposition resulting in increased leaching of heavy metals from terrestrial ecosystems
Redox Potential	5 Drainage of wetlands with high contents of sulfide minerals	6 Submerged riparian woods as sink for excess nitrate before river discharge; man-made disturbance of woods causing increased discharge of nitrate to rivers	7	8 Low redox conditions in water resulting in sediments as a sink for heavy metals; High redox conditions resulting in sediments as a source of heavy metals

duration of waterlogging in the riparian zone; and 3) Deforestation of riparian forests that may lead to a decreased amount of organic carbon needed by bacteria in the denitrification reaction.

Redox Potential/Toxic Materials Accumulation (Box 8)

In estuarine and coastal marine ecosystems, we have described in the previous discussion how contaminated sediments may serve as a sink for toxic materials under conditions of low redox potential, and how they may serve as a source for the release of these materials under conditions of high redox potential. Also, we have seen how the dredging of anoxic, contaminated sediments, and disposal in aerobic environments may lead to remobilization of the sediment-bound toxic materials.

5.4. Combined Primary and Secondary Interactions: Table 8

Combining Tables 6 and 7 yields Table 8. We may observe in the expanded matrix that in addition to the primary interactions identified earlier, several other development/environment interactions are revealed. Fossil fuel combustion is indirectly linked to the mobilization of heavy metals from terrestrial soils as a result of the acidification of the soils (Box 4).

Agricultural activities, in addition to the primary interactions, are also linked to several other effects through intermediate interactions. Soil and lake acidification may occur when wetlands with high concentrations of sulfide are drained for agricultural purposes (Box 5). Liming augments the ability of agricultural soils to adsorb certain heavy metals and pesticides, and conversely, the cessation of liming may cause the adsorption reservoirs in soils to shrink (Box 6). River impoundment, land drainage, or deforestation of riparian wet land zones may cause increased nitrate discharges to rivers (Box 7). Current practices of over-fertilization affect the accumulation of toxic metals in aquatic sediments by contributing to the low redox potential that favors accumulation (Box 8).

Similarly, industrial, commercial, and domestic activities, in addition to directly generating toxic materials, also affect the accumulation of toxic chemicals in aquatic sediments by influencing the redox conditions of the waters above these sediments (Boxes 12 and 16). They do so by directly discharging into these water bodies, large quantities of organic wastes with high CODs.

Table 8. Development/Environment Interactions[a]: Combined Primary and Secondary Interactions

Consequences / Sources	Buffering Capacity	Sorption Capacity (Agricultural Soils)	Redox Potential	Toxic Materials Accumulation
Energy Use	**1** Acid deposition	**2**	**3**	**4** Heavy metals;PAHs ━━━ Increased leaching of metals from terrestrial ecosystems as a result of acidification of soils
Agricultural Activities	**5** Liming ━━━ Drainage of wetlands	**6** Phosphate application;cadmium, other heavy metals, pesticides ━━━ Liming augments sorption capacities; cessation of liming will diminish them	**7** Over-Fertilization by nitrate, subsequent discharge to water ━━━ Disturbance of riparian woods as sink for nitrates	**8** Pesticide runoff ━━━ Accumulation of heavy metals in sediments under low redox conditions caused by nitrates leaching to water bodies
Industrial Activities	**9**	**10**	**11** Discharge to water of organic carbon chemicals with high COD	**12** Heavy metals;toxic organic chemicals ━━━ Accumulation of heavy metals in sediments under low redox conditions caused by discharge of chemicals with high COD
Commercial and Domestic Activities	**13**	**14**	**15** Discharge to water of organic carbon chemicals with high COD	**16** Heavy metals; toxic organic chemicals ━━━ Accumulation of heavy metals in sediments under low redox conditions caused by discharge of chemicals with high COD

[a] Text under double lines describes secondary interactions

6. IMPLICATIONS FOR ENVIRONMENTAL CHANGES IN THE FUTURE, INCLUDING SURPRISES

One way to imagine how the environment may change in the future is to examine the activities that could, directly or indirectly, drive the changes (here described as changes in the CEIs), and to ask how those activities might evolve in the future. Table 8 was constructed in order to facilitate that task. Another approach might be to start from the impact end of the assessment. Here one asks: within which environmental settings are changes in the CEIs most likely? Then, working backwards, asks whether these environmental settings are possible, and if so, under which activities or circumstances could they be realized? Both approaches are used here interactively .

Earlier, I described how the redox potential was very much governed by the limited concentration of molecular oxygen in water. I cited two examples, the acidification of Lake Blamissusjon, and the nitrate trap provided by the water-logged riparian woods, to illustrate how the chemical response in soils could change dramatically, depending on whether they were water-logged or drained. The two cited examples were local occurrences, and in and of themselves, perhaps not very important on a continental scale. However, as shown schematically in Figure 24, they do suggest the potential importance of wetlands in protecting water bodies from pollutants of nitrogen and sulfur. The importance of this function of wetlands could be magnified in the future if there were broad scale changes in the hydrological cycle in Europe such that wetlands dried out, and dry lands became wetter due to the lowering and raising of water tables in response to shifting seasonal and annual patterns of precipitation and evapotranspiration. And if these changes were accompanied by broad scale increases in the acidification of soils, there could be major shifts in soil chemistry, with potentially important impacts on the environment. Much has been written about the leaching of heavy metals from terrestrial soils as a result of acidification. However, as was shown in Figure 22, mobilization depends not only on pH, but is equally affected by the redox potential.

It is beyond the scope of this paper to delve deeply into a discussion on future climatic change in Europe. Suffice it to say here that even though we cannot yet predict precisely how the climate in Europe may change in the next century, the best current models appear to lend credence to the possibility of wide-spread changes in European hydrology. Figure 25 shows the changes in summer soil moisture based on a model developed by Manabe and Wetherald (1986), assuming a doubling of the current CO_2 levels.[9] One may observe broad-scale reduced moisture levels for nearly the entire continent. Reductions in moisture of up to 50% were calculated for Southern Europe, and as much as 30% in Northern Europe. Understanding the implications of such large regional reductions in soil moisture on the soil's redox potential could be of critical importance. Will large numbers of lakes acidify after the fashion of Lake Blamissusjon? Will nitrate levels discharging into rivers increase as riparian wetlands dry out? In planning a research agenda for long-term ecological substanability in Europe, these and related questions may well be considered for more detailed investigation.

I describe below, six potential environmental changes. These are based on the information in Table 8, the analyses conducted in the previous sections of this paper, and finally, by simply thinking about the sensitivities of particular CEIs. The first three listed are changes induced by primary (direct) interactions between chemical inputs and ecological systems, and the last three are from secondary (indirect) interactions. Because most of the changes occur within a background of improving environmental conditions, they may appear as surprising, or perhaps even paradoxical, at first glance, but are actually quite

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[9]According to current estimates, the equivalent of a doubling in CO_2 could occur as early as 2030. This assumption is based on a 50% rise in CO_2 by that time, as well as an increase in the so-called "greenhouse" gases, that may contribute the equivalent of a 50% rise in CO_2 by 2030.
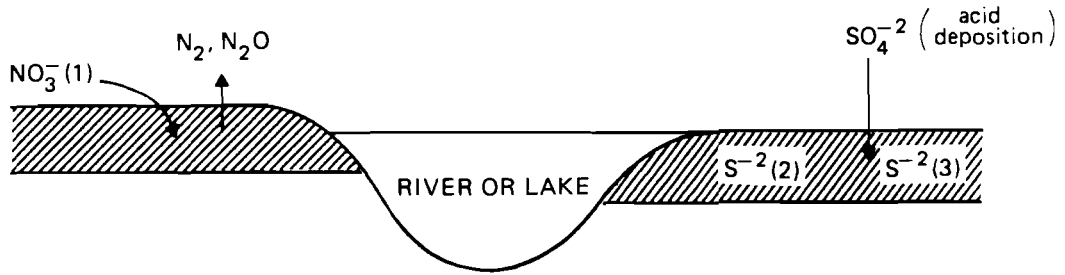
Wetlands as a Sink for Nitrate and Sulfate

(a)
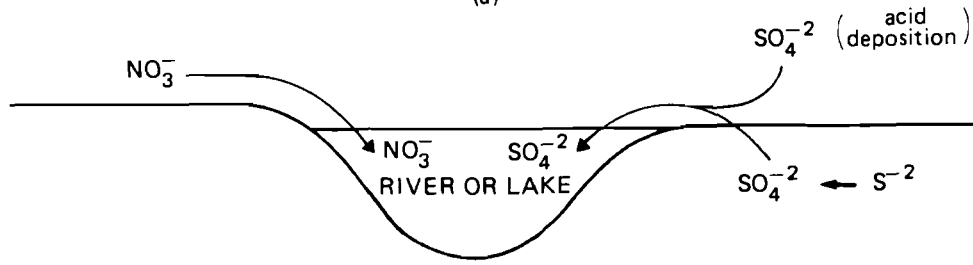
Dry Land as a Transporter of Nitrate and Sulfate

(b)

[1] Nitrate from runoff of nitrogenous fertilizer

[2] Sulfide minerals from former marine sediments

[3] Sulfide reduced from sulfate inputs of acid deposition

Figure 24 (a) Ability of wetlands to buffer against nitrate and sulfate inputs to water bodies. Nitrate is reduced to molecular nitrogen (N_2) or nitrous oxide (N_2O), both of which are vented to the atmosphere. Sulfate (SO_4^{-2}) is reduced to sulfide (S^{-2}), which forms an insoluble precipitate in wetland soils. (b) Under conditions where wetlands become dry, none of the protective reducing reactions occur. In addition, sulfides that were stored in wetland soils may become oxidized and leach into water bodies. Shaded area indicates region of wetlands.
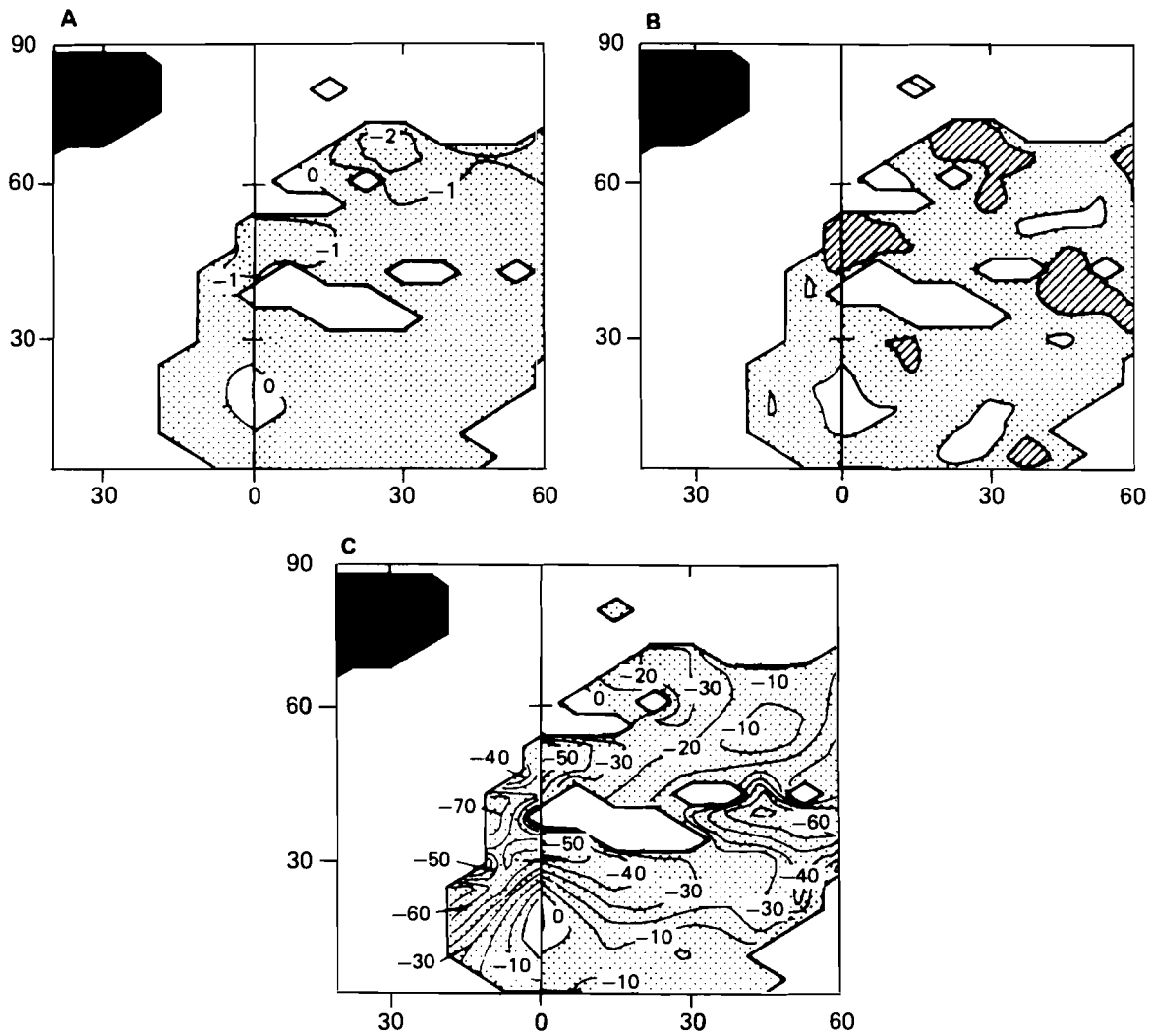
Figure 25   (A) Geographical distribution in Europe of the change in soil moisture (centimeters) in response to a doubling of CO_2 for the period from June to August. Shading indicates regions where the CO_2-induced change is negative. (B) Statistical significance of the CO_2-induced change in soil moisture shown in (A). Areas shaded with lines are regions where the negative soil moisture change is statistically significant at the 10%level. (C) CO_2-induced change in soil moisture expressed as a percentage of soil moisture obtained from the normal CO_2 experiment. Source:Manabe and Wetherald, 1986.

understandable in the context of the linkages described in the previous sections. Again, since I have discussed most of these changes in some detail in previous sections, I will not elaborate further in those cases. For more specific details you may refer to the relevant sections.

6.1. The Continued Acidification of Soils, Even in an Era of Reduced Acidic Emissions.

According to the analysis of Alcamo et al. (1987), current planned reductions of emissions of SO_x in Europe by 30% relative to 1980 values will not be sufficient to prevent wide-scale and continuing acidification of forest soils in Central Europe by the year 2040. As shown in Figure 6, as much as 60% of the soils could have pHs less than 4 by that time. The problem is that although the reductions will certainly slow down acidification, the depletion of buffering capacities will still occur at rates more rapid than the rates at which soils can replenish their capacities.

6.2. The Saturation of Soils by Phosphate, and Subsequent Leaching of Phosphates into Ground and Surface Waters, Leading to a New Wave of Eutrophication of European Water Bodies.

Currently in the Netherlands in areas of enormous livestock feedlots, phosphate saturation has already occurred where large excesses of livestock manure have been applied in sandy soils of adjacent farms. In other areas of Europe phosphate inputs, though not as large as in the Dutch example, are nonetheless substantial, and about half the phosphorous applied appears to be stored in the soils. Calculations by Behrendt (1988) show that over the next 90 years 1 to 2 meters of agricultural soils could be completely saturated, and leaching may occur in areas with high water tables. (See Figure 12.)

A major problem with phosphorus is that no natural process comparable to "nitrogen-fixation" exists. Hence, the possibility for a technological breakthrough in improving the efficiency of plants for phosphorus uptake will not be available in the foreseeable future. Accumulations may be slowed significantly, however, if official recommendations of agricultural extension services are adopted. Then the application level is adjusted on the basis of phosphorus availability in the soil. This practice would entail, however, regular soil-sampling analysis on the farm level.

6.3. A Continuation of Anoxic Conditions in Coastal Waters, Resulting in Episodic Fish-Kills and Emissions of Hydrogen Sulfide.

As demonstrated in Figure 18, by the early 1980s, unprecedented episodes of fish kills and $H_2 S$ generation were observed off the Danish coast. The same phenomenon has been observed in the Gulf of Saronik near Athens. It is possible that similar episodes may spread to other regions of Europe in the future. This may occur even after a significant improvement in sewage treatment. In fact the percentage of the population of Denmark served by waste-water treatment plants increased from just over 50% in 1970, to about 90% in 1983. Unlike the episode off the Greek coast, which was the result of the discharge of sewage wastes,[10] the Danish episode was caused by large discharges of nitrate fertilizers into the coastal areas. Since the major rivers emptying into the North Sea contain nitrate

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[10]Greece is exceptional in that as of 1980 hardly any of the population was served by sewage treatment. For most of the OECD countries there has been a considerable increase in sewage treatment since 1970 (OECD, 1985).

levels 30 to 40 times higher than background levels, there will have to be significant reductions in the runoff of fertilizers in the future in order to prevent anoxia in the coastal waters. The southern and eastern areas of Europe may be particularly vulnerable in this regard, since in many of these areas agricultural activities are still expanding. (In western Europe they have peaked and will probably decline sharply in the future.)

Furthermore, the increase of tourism along the Mediterranean and Adriatic coasts has increased markedly in recent years. The sea-side towns in these areas often do not have adequate sewage systems to treat the huge increases of wastes caused by tourism during the summer months.

6.4. The "Bleeding" of Toxic Metals from Contaminated Sediments in an Era of Vastly Improved Water Quality.

The previous discussion indicated that in terms of accumulations of toxic materials in the sediments of rivers, estuaries, and coastal areas (and conversely the potential for release from these sediments), the status of the redox conditions in the overlying water columns may be at least as important a factor as are the direct accumulated inputs of pollutants.

If current trends continue in western Europe, there will be major reductions in organic carbon inputs to the large river systems. Virtually all the countries in this region have vastly expanded their capacities for waste water treatment in the last two decades (OECD, 1985). Also, at least for some of the heavy metals such as mercury and cadmium, there seem to have been significant reductions over the last decade in direct discharges into major rivers such as the Rhine (OECD, 1985). However, because of the huge excesses of nitrogen fertilizers still discharging into these rivers, the low redox conditions still prevail. If solutions are found for reducing water pollution from nitrate, there should be a significant improvement in water quality in western Europe. Possible significant reductions may occur as a result of the following: better, more efficient methods for nitrogen fertilizer application (See, for example, Fleischer et al., 1987); the discovery, through biotechnological research, of nitrogen-fixing cereals; the large-scale cut-back of agricultural activity due to overproduction in the EC countries.

However, if the quality of these waters were to improve significantly, the new environment would be a combination of clean waters overlying heavily contaminated sediments. We have noted in the previous discussion that under these conditions the sediments could be a source of, rather than a sink for toxic chemicals. (See Figure 20 and the ensuing discussion.) Preliminary studies indicate that the sediments in these conditions will purge themselves by releasing metals at various rates, possibly for many years into the future. Furthermore, a significant fraction of the remobilized metals may be in a form far more available to biota than the form under which they were first deposited into the sediments.

The above discussion is not to suggest that we should avoid cleaning polluted water courses. Rather, in making management decisions about clean-up programs, it is very important that the decision maker uses available knowledge to understand at least some of the contingencies, surprises, trade-offs, and risks inherent in the final plan of action. Only then will such decisions be informed, and the quality of thinking among the decision makers maximized. For example, perhaps the most robust decision would be to set up, as a concurrent activity to the clean-up, a system for monitoring toxic metal concentrations in selected water bodies in order to seek answers to important questions such as the degree of bioaccumulation, the potential impacts on human health, and the hydrological and physiochemical conditions under which the effects of toxic releases from these sediments would be most detrimental.

6.5. The Release of Toxic Metals from Agricultural Soils Upon the Cessation of Liming.

We have demonstrated that liming of soils may serve to amplify the soil's capacity to adsorb heavy metals. It is possible, perhaps even likely, that in the coming decades large tracts of agricultural land in Europe will be abandoned for agricultural purposes, and liming discontinued. With the exception of acid deposition, liming is probably the major anthropogenic activity affecting soil pH. When soils are no longer limed, there could be a significant, and rapid decrease in pH. This effect will be aggrevated in areas receiving high levels of acid deposition. Because some of these soils have been the recipient of cumulative doses of heavy metals and pesticides over several decades, the sudden decline in pH may cause large discharges of these metals into ground and surface waters. Such events could trigger serious ecological and human health problems. Given that agricultural lands, at least in western Europe, could be decreased by 20% or more, the effects could be widespread on a regional basis.

6.6. Environmental Changes Occurring as a Result of Changes in Soils' Redox Conditions Due to Drying Up of Wetlands, or the Moisturization of Dry Lands.

We have seen in the development of our matrix, an example in a region of northern Sweden whereby drainage of watershed soils high in sulfide minerals caused the severe acidification of a lake and its drainage basin. The cause of this event was the exposure of the sulfide minerals to atmospheric oxygen, resulting in the oxidation of sulfide to sulfuric acid.

We have also noted how the nitrogen cycle can be significantly affected by wetland areas, which may serve as nitrate traps, thus buffering rivers from high inputs of nitrate from agricultural lands in the drainage basin. There are no doubt many other examples of how changing redox conditions in the soils may influence the quality of soils and surface waters. The two cases cited here are merely by way of example.

Moreover, redox conditions in the soil strongly influence the emissions of trace gases to the atmosphere (G. Zavarzin, Institute of Microbiology, U.S.S.R. Academy of Sciences, Puzchino, personal communication, 1986). For example, water-logged soils may emit significant quantities of N_2O and methane, which are trace gases that have an important influence on global climate.

Given that there may be large changes in the hydrological conditions in Europe in the next century caused by global climate change, there may also be broad-scale changes in redox conditions in the soils as water tables rise or fall. Falling water tables will change the soil chemistry from one governed by reducing conditions to one governed by oxidizing conditions in some of the areas now submerged or water-logged . Conversely, rising water tables will change the soil chemistry from one dominated by oxidizing conditions to one dominated by reducing conditions in some areas now dry.

From our two examples, we know that under certain circumstances lowering of the water table could cause lake acidification and increased runoff of nitrates into rivers. Would there be another wave of acidification under the new hydrology? A first step might be to overlay a current map of European soils high in sulfide minerals with maps showing possible changes in hydrology. Potentially vulnerable areas would be those showing reduced water availability in areas of high concentration of sulfide minerals. Will the drying up of wetlands in agricultural regions cause a new wave of nitrate pollution in water courses? Again a first step might be to overlay a current map of the wetlands of Europe, with maps of current agricultural activity and maps of possible new hydrologies.

Moreover, since we have seen that the mobility of toxic metals is greatly affected by the redox potential, there may be particularly vulnerable areas where increased leaching of metals can occur, as for example, from toxic waste land fills, currently safely stored in anaerobic environments.

7. IMPLICATIONS FOR A MONITORING STRATEGY

One goal of this paper has been to demonstrate how activities of socio-economic development in the areas of energy use, agriculture, industry, and commercial and domestic consumption affect certain capacities of soils, waters, and sediments, and how the causal activities may be displaced in time and space from the manifestation of environmental effects. As noted earlier, Brooks (1986) has cautioned that the ultimate danger of such a relationship is that the activities, for which societies generally reap rapid short-term gratification and economic benefit, tend to become entrenched over time, making it difficult for adjustment or change by the time the disbenefits become known. Moreover, even if adjustments can be made willingly, it may be too late if the particular degradation is not reversible.

Another goal implicit in the analyses presented in this paper is the question of our obligations to future generations for the responsible stewardship of the environment. (See for example Brown Weiss, 1984.) Most of the examples presented in the previous sections might be described as environmental "time bombs." The explosion may occur in the generation of our grandchildren, but the ticking of the clock has begun in our generation, as we contribute to the year by year accumulations that will lead eventually to rapid threshold responses.

Thus, one of the major needs of long-term strategic planning for the ecological sustainability of Europe is a more efficient monitoring system for early warning of potential environmental threats. By early warning I mean identification of a problem early enough to allow sufficient time for society to mobilize an effective response. I offer here a few ideas that hopefully will help toward that goal.

7.1. Indicators

The first step in designing such a system is to define a set of indicators that will provide reliable early warning of potential environmental changes. As an example, we may again refer to the previous discussion on the acidification of Big Moose Lake. (See Figure 3 and the ensuing discussion.) What would have been a proper monitoring strategy to have foreseen, say in the year 1920, the acidification of the lake that was to occur around 1950? Certainly, measuring the pH of the lake alone, or even the pH, the sulfur emissions up-wind from the lake, and the fish species populations would have been insufficient to have foreseen the acidification. The key indicator was the buffering capacity of the watershed soil. That was the slow variable whose depletion over the decades since 1880 was occurring as a result of cumulative alterations of base cation supply that would appear as minor if viewed over a short time horizon. In fact, it was the only indicator between 1920 and 1950, for which a change would have been observed. Emissions of sulfur were nearly constant over this period, as were the pH of the lake, and the fish species populations. By the time changes in pH and fish populations were observed, it would have been too late to reverse the effect.

From this example we can clearly understand the overriding importance of knowing precisely what to measure when designing an effective monitoring program. As shown in Figure 26a, for an ecological change that is delayed in time with respect to the source of change, there is generally no direct linkage between cause and effect. Rather, the source of pollution acts on the environment through some intermediate step. Moreover, this step must generally involve either a depletion of some capacity, or alternatively, an accumulation of some pollutant. It is this depletion or accumulation that appears as a slowly changing variable in time, and it is this variable which must be monitored.

As illustrated in Figure 26b, in more complex cases there may not only be one, but two or several intermediate steps. In this situation, it will be crucial to monitor the rate-determining step, and to have information about the linkages between all the intermediate steps. In the example shown in Figure 26b, monitoring the depletion in buffering
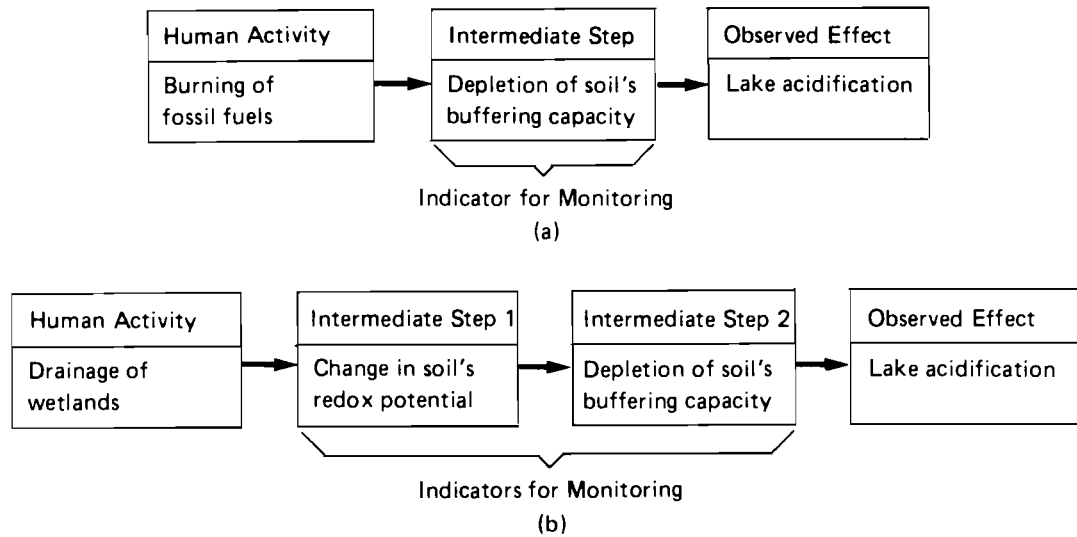
Human Activity	Intermediate Step	Observed Effect
Burning of fossil fuels	Depletion of soil's buffering capacity	Lake acidification

Indicator for Monitoring

(a)

Human Activity	Intermediate Step 1	Intermediate Step 2	Observed Effect
Drainage of wetlands	Change in soil's redox potential	Depletion of soil's buffering capacity	Lake acidification

Indicators for Monitoring

(b)

Figure 26   (a) Illustration of simple linkage between human activity (cause), and the observed effect for the case of acid deposition and lake acidification. (b) Illustration of more complex linkage for the case of drainage of wetlands and lake acidification.

capacity of the soil may provide warning of the impending acidification of the lake in the watershed, but we would not be able to connect the depletion of buffering capacity to land drainage, unless we knew the linkages between land drainage, changing redox potential, and soil acidification.

Given these considerations, I suggest three minimum criteria that must be met for an indicator to be useful in a monitoring program for early warning:

1. The indicator must be expressible as a measurable parameter that is sensitive to small incremental changes over time.

2. There must be a mechanistic linkage established between the source of pollution, the indicator, and the final effect. For multi-step processes involving several intermediate linkages, the coupling between the indicator and the other intermediate processes must be understood.

3. The indicator must not measure the threshold effect itself, but rather, the changes that may trigger the effect.

7.2. Lessons from the Most Vulnerable Areas

In designing a program that will provide early warning of sudden ecological changes, one logical place to start looking for such changes is in the most vulnerable areas. As we have seen, two factors determine vulnerability: 1) the level of inputs of polluting chemicals; and 2) the size of the reservoir for storing or depleting them.

The history of the acidification of European soils and waters demonstrates both the potential utility of this approach, and the lost opportunity in foreseeing the spread of acid deposition from initially a very small region in Southern Scandinavia to most of the

central part of Europe. Central Europe experiences the highest inputs of acid, although its soils have been fairly resistant to acidification. Southern Scandinavia has experienced moderate inputs of acidification, most of it imported from up-wind sources in the U.K., Germany and elsewhere. However, its soils possess among the lowest buffering capacities on the continent. Hence, according to the two criteria given above, both Southern Scandinavia and Central Europe were prime candidates for vulnerability to acid deposition. As shown in Figure 27, the direct effects of acidification were first observed in Scandinavia. The earliest signs appeared in the 1920s as reduced stocks of salmon in rivers in southern Norway that were previously prolific fishing rivers. It wasn't until decades later that direct effects were observed in Central Europe.

The experience in Scandinavia could have provided warning of what would inevitably happen in Central Europe had the early signs been heeded. Indeed, as has been pointed out by Paces (1985), mounting evidence within Central Europe of deleterious effects from acid deposition was largely ignored:

Nobody worried about acidification. The term was unknown. The first practical acknowledgment of the problem came when farmers began to place lime on their fields. This process was in most cases sufficient to neutralize agricultural acidification.

Ten years ago, after about 150 years of acidification, we in central Europe were still concerned with the eutrophication of lakes and rivers and not with acidification. We did not observe any remarkable systematic decrease in the pH of surface waters except in some high-altitude lakes. We measured a systematic increase in sulfate and nitrate in runoff and noted that topsoil was losing humic substances. In trees we observed the spread of parasitic disease and increasing damage caused by winds and snowfall. Still nobody seemed to be concerned with acidification.

Meanwhile, in Scandinavia, where atmospheric acid pollution is only a small fraction of that found in central Europe, scientists became seriously concerned with this problem upon discovering drastic decreases in the fish populations of acid lakes. The problem was perceived as an international one because much of the acidic input was produced outside Scandinavia's frontiers Nevertheless, acidification was not much of an issue during the 1972 United Nations Environment Conference in Stockholm.

One lesson to be learned from this experience is that perhaps, as a general principle, we should pay closer attention to what appears to be novel environmental occurrences that appear as localized events, but which may in fact be harbingers of future problems on a grander scale. If these events are good natural experiments or test cases for what is to come, then perhaps we should find out why the effect appeared at the particular location, and try to discern whether the episode is indeed only of local significance, or whether the same event could happen elsewhere under different conditions. In this paper, we have noted that in recent years, extraordinarily high levels of phosphate have been applied to soils of local farms in the livestock feeding areas of the Netherlands. The inputs are so high that these soils are already experiencing saturation of phosphate sorption capacities. We suggested that the same problem could occur in other parts of Europe, where, although levels of application may not be as high, accumulations over longer periods of time could lead to the same deleterious effects.

Would it not be a wise strategy, therefore, to develop a European-wide vulnerability map for phosphate sorption capacities? Dutch investigators have already developed a method for obtaining an index of vulnerability utilizing information readily obtained from standard soil maps (Schoumans et al., 1987). Such a map could be overlayed by other maps showing the intensity of phosphate application and the depth of water tables, in

6.0

5.5

pH

5.0

4.5

1900   1920   1940   1960   1980   2000   2020   2040   2060

regional time lag

beginning of
observed effects
in Scandinavia

beginning of
observed effects
in Central Europe

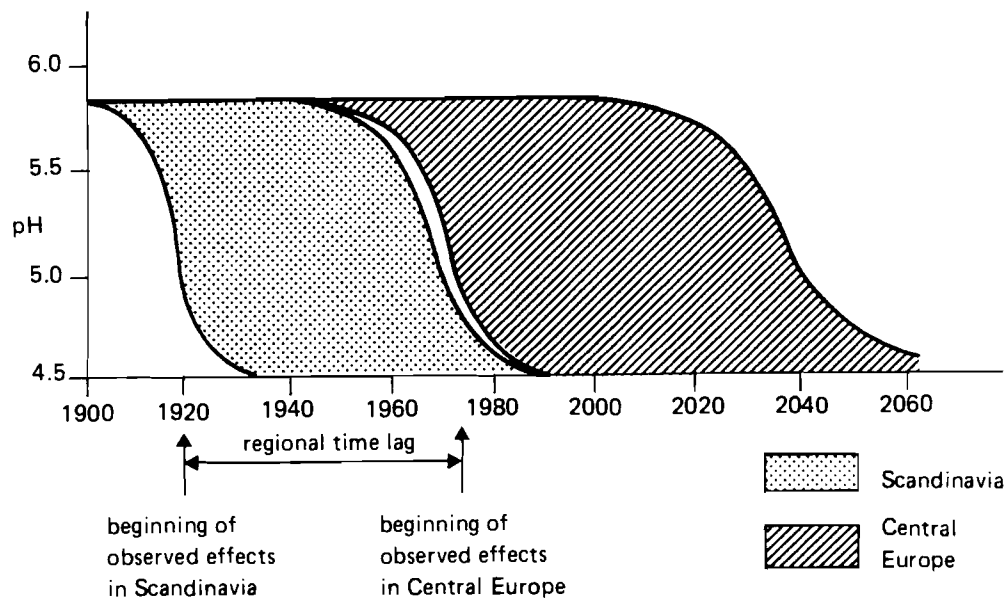Scandinavia

Central
Europe

Figure 27   Time horizons of effect of acid deposition on acidifications of soils and lakes in Scandinavia and Central Europe, indicating the lag time in response of Central European soils of about 50 years relative to the response of Scandinavian soils. Central Europe includes West Germany, Switzerland, Austria, Hungary, Czechoslovakia, Poland, and East Germany, after Alcamo et al., 1987.

order to determine the location of the most vulnerable areas. Regular monitoring of the soils in those areas could provide a valuable assessment of the timescale over which effects may be manifested. This information could then be used more widely to assess the magnitude of the problem in other, less vulnerable areas of the continent, and perhaps to foresee problems in the future, given certain scenarios of development.

Likewise, the estuaries and coastal areas of the North Sea, fed by rivers transporting pollutants from some of the most heavily industrialized and intensively cropped areas in the world, have become major sinks for toxic wastes, and worrisome ecological changes have already been observed. What are the trends in other coastal regions of Europe? Are they prone to similar degradation if they follow a similar development path? Can we use the knowledge gained from the analysis of the circumstances causing the fish kills off the Danish coast in the early 1980s to foresee how and where similar events could be repeated? Is the Adriatic coast similarly threatened, especially in summer by large discharges of untreated sewage wastes caused on the one hand by the ever-increasing flow of summer vacationers to coastal towns, and on the other by sewage treatment facilities totally inadequate to service the expanded summertime populations?

7.3. The Bottom-up Approach

It is not always possible to uncover vulnerabilities by looking to areas with high inputs of pollutants, or areas that are particularly pollutant-sensitive. This is especially true when attempting to anticipate problems that do not currently exist. In these cases the "bottom-up" approach might be particularly useful. (For further discussion, see also Parry and Carter, 1987.) Here, the focus is on the impact, and the analyst asks two questions: 1) To what factors is the impact particularly sensitive? and 2) Under what scenarios could these factors become a reality? Figure 28 illustrates how the method might be applied to the critical environmental indicators highlighted in this report.

The five listed "sensitive" factors and the scenarios under which these factors could become important are based on the discussions in the previous sections. Changing moisture conditions due to climatic change could have a major impact on the redox conditions in the soils of Europe. The release of heavy metals in contaminated sediments of estuaries and coastal areas is sensitive to two factors: 1) the redox conditions in the overlying waters; and 2) the mechanical disturbance of the sediments. It is possible that both factors will gain in importance in the future, as water quality generally improves, and as sea level rise and the increased frequency of storms causes increased turbulence in the sediments of the coastal and estuarine areas. We have seen that sorption capacities are very sensitive to acidity, and acidity may increase in the future in soils of abandoned farm land if the practice of liming these soils is halted. Finally, acid deposition itself, the distribution of which is dependent on patterns of rainfall and wind direction, may also be affected by climate change if these patterns change markedly.

The advantage of the "bottom-up" approach is that it raises questions that might otherwise not have occurred to the experts studying the various environmental problems from the "top-down." In so doing, it may help to channel some of the ongoing research and monitoring programs in climatic change, water quality, and agricultural pollution in a direction that is more directly applicable to long-term impacts on the critical environmental indicators.

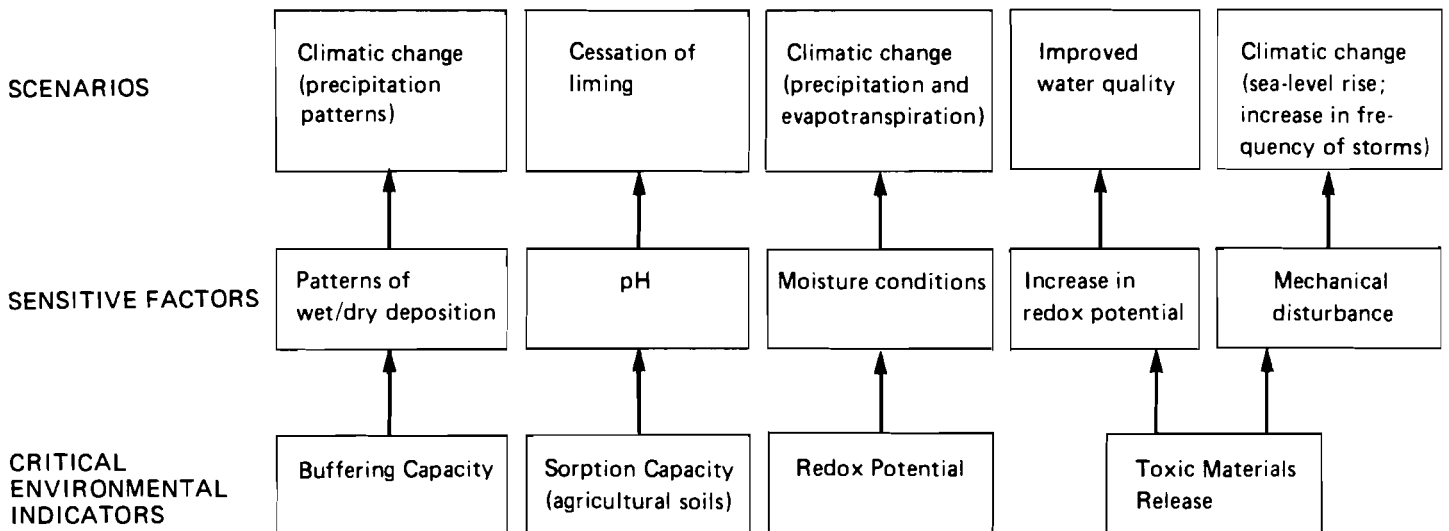| SCENARIOS	Climatic change (precipitation patterns)	Cessation of liming	Climatic change (precipitation and evapotranspiration)	Improved water quality	Climatic change (sea-level rise; increase in frequency of storms)
SENSITIVE FACTORS	Patterns of wet/dry deposition	pH	Moisture conditions	Increase in redox potential	Mechanical disturbance
CRITICAL ENVIRONMENTAL INDICATORS	Buffering Capacity	Sorption Capacity (agricultural soils)	Redox Potential		Toxic Materials Release

Figure 28   Illustration of the bottom-up approach.

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